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THE LATTICE AND ELECTRONIC SPECTRUM OF DIAMOND

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Received March 10, 1942

(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

1. *Introduction*

IN a previous communication to these *Proceedings*, the author (1941, I) showed that, when excited by suitable radiations, diamond exhibited a characteristic fluorescence. The principal features of the spectrum of the fluorescent light consisted of a sharp band at 4156 A, followed by a number of broader bands on the long wavelength side of that band. Though varying in intensity to a considerable degree among different specimens, the nature of the spectrum was the same in all the crystals studied. In a subsequent paper (1941, II) the existence of two distinct processes in the emission of light was brought out, one an instantaneous *fluorescence* and the other a considerably delayed *phosphorescence*, and the spectroscopic features in the two cases were recorded. The study of absorption of light in diamond was the subject of a further paper (1941, III). There it was shown that the band at 4156 A occurred also in absorption, together with a system of bands on the short wavelength side, forming a mirror-image pattern of the fluorescence spectrum. Various other points of interest of a general nature regarding the fluorescence and absorption phenomena, like the relation between intensities in emission and absorption, the effect of temperature and of exciting wavelength, were also recorded in the above papers.

An important result which followed from these earlier studies was the fact that the entire spectrum in fluorescence and absorption stood in the closest relation to the 4156 band. The pattern of bands was found to be the result of combinations of this electronic frequency with vibrational frequencies, which in turn were found to correspond to infra-red frequencies of diamond, observed notably among others by Robertson, Fox and Martin (1934). A certain amount of unresolved structure was noticed in the individual fluorescence and absorption bands even then, and it was realised that a finer and more accurate analysis of the spectra would lead to a better understanding of the vibrational spectrum of diamond.

The temperature studies made it evident that this purpose could be achieved by narrowing the principal band, by cooling the crystal to the lowest available temperature, and resolving the spectrum further by the use of a high dispersion spectrograph. The investigations which are described in this paper deal with the new results obtained by these methods, and have helped to confirm the earlier conclusions, and lead to the derivation of the lattice spectrum of diamond.

In addition to the band system referred to above, which was closely connected with fluorescence, the author was able to find several new absorption frequencies farther in the ultra-violet over and above a few reported by Robertson *et al.* By the use of low temperatures and higher dispersion, this region also was subjected to a systematic study. Unlike the 4156 band, which was ascribed to the active centre responsible for fluorescence, the sharp bands in the ultra-violet were found to be present in all crystals with intensity practically independent of the differences between different crystals. These were therefore ascribed to transitions connected with the electronic structure of diamond proper. The present work at low temperature revealed the existence of still more detail, and it has been found possible to record more than 25 distinct absorption frequencies in the ultraviolet spectrum.

2. *Experimental Technique*

The material available for study has been described in a previous paper (I, p. 485). The experience gained in earlier investigations, made it possible to select the right crystals suitable for the present purpose without difficulty. For observations on fluorescence a highly fluorescent crystal (called D_7 in the previous papers) was employed. Absorption studies required the use of a number of crystals, employed edgewise, as well as flat, to obtain thicknesses varying from 20 mm. to 0·5 mm. The resolution achieved in each particular region was dependent entirely on the thickness best suited for the intensity of absorption in that region.

The spectrograph employed was a Hilger quartz Littrow spectrograph (E_1) with a dispersion of 4·5 A in the 3000 A region, changing to 14 A/mm. in the 4100 region. The use of this comparatively slow instrument required an experimental technique in which the crystals could be held at low temperatures for long intervals of time. The necessity for frequent changes of the crystals employed, called for an easily demountable arrangement. An apparatus suitable for such a purpose has been described by the author (1941, IV) in connection with the study of the Raman spectrum of diamond at low temperatures, and the same apparatus was adapted for the present work by the provision of quartz windows. Briefly, in this arrangement, the crystal was embedded in a copper block and fixed outside the bottom of a long thin-walled brass cylinder, designed to contain liquid air. An outer jacket of glass with quartz windows, with a putty seal between metal and glass, was kept continuously evacuated, forming a vacuum jacket round the metal cylinder. A Cenco pump in good condition was found adequate for maintaining the vacuum, and the keeping quality of the flask was sufficient to enable a day's exposure with 2 litres of liquid air. The crystal was therefore held in intimate contact with the container, but otherwise in good thermal insulation in vacuum, so that it attained the requisite temperature a few minutes after introducing liquid air. A fine copper-constantan couple in contact with the crystal enabled the temperature attained by the crystal to be checked, especially in the attempts at securing temperatures lower than that of liquid air.

For exciting fluorescence, the 3650 group of lines from a quartz mercury arc filtered through Wood's glass was employed, giving complete freedom from mercury lines in the region of fluorescence. For absorption, the sources of continuous spectrum used were the over-run incandescent lamp, and the hydrogen discharge as in the previous work.

Absorption pictures were also obtained at solid CO_2 temperature and room temperature in some cases. Using a convenient crystal with which absorption could be recorded in a few seconds, pictures were obtained at a temperature of 22° lower than liquid air. This was secured by boiling the liquid air at reduced pressure in the metal container, using a large capacity pump.

3. *New Results in Flourescence*

A well-exposed picture of the fluorescence spectrum at liquid air temperature is given in Fig. 1*a*, Pl. VII. It can be seen there that the principal band is very intense and sharp. The peak of the band as determined by a microphotometer curve was found to be 4152·2 A. The region covering the next two bands stands out prominently from the remaining bands in the visible region, in having a striking amount of detail inside the bands, and in intensity. An enlarged picture of this region is given in Fig. 2 where the most prominent features are indicated by arrows. The measurements of these details are given in Table I with their description, and the different regions are numbered as in the previous papers for convenience in describing them below.

The sharpness and high intensity of the principal line at 4152* has already been mentioned. The next region numbered ii is one of extreme faintness.

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* The figures in the text indicate wavelengths in A.U.

The limits lie between 4175 and 4230. In between, there are at least three discrete lines at 4183, 4197 and 4206. The strongest of these is a very sharp line at 4206, which however is also the position of a faint absorption band (see section 12), and therefore an electronic frequency similar to the 4152 band.

The next region is the band numbered II in the Table. This has a remarkably sharp edge at 4246 and terminates with a sharp edge at 4292. In between, there is a sharp rise of intensity at 4273 dividing this region into a band between 4246 and 4273, and a band of higher intensity between 4273 and 4292. There are vague indications that these two groups have further breaks within them.

The details of the region marked II*a* were overlooked in the previous work, partly due to the presence of the 4358 and companion lines of the mercury spectrum, and to the fact that they were weak in comparison to the neighbouring bands. Four distinct lines of about the same breadth as the 4152 line are present in this region at 4304, 4323, 4334 and 4349, of which the 4334 and 4349 lines are the clearest as can be seen without difficulty in Fig. 2.

The band III is particularly interesting as an intense band with an edge which stands out most prominently in the entire spectrum. Here again there are 3 discrete lines at 4360, 4380 and 4395 super-imposed on a heavy continuum. The limits of the band are between 4357 and 4397, the latter being extremely sharp and intense. The sharpness of this edge is presumably due to the presence of the line with its middle at 4395.

Before passing on to the remaining bands, it should be mentioned that the impression gained from a close study of the bands is that the presence of discrete lines at the limits is responsible for the sharpness of the edges. This point is raised again when dealing with the absorption results.

The remaining bands farther in the visible region have rather ill-defined limits and do not show any new detail. The measurements in the present work, however, are more reliable because of the higher dispersion employed, and the revised values are given in the Table.

4. *Results in Absorption*

It has been remarked already that corresponding to every band in fluorescence, there is present in absorption also a band displaced from the principal band by an equal frequency shift. This relationship has been confirmed in a much more rigorous fashion in the present work, where the

TABLE I

FLUORESCENCE						ABSORPTION				
No.	Wave-length A.U.	Intensity	Description	Frequency cm.$^{-1}$	Frequency difference	No.	Wave-length A.U.	Description	Frequency cm.$^{-1}$	Frequency difference
						I	4206*	Faint line	23769	..
I	4152*	10	Sharp	24077	..		4152*	Close doublet	24077	
ii	4175		Limit	23945	(*132*)	ii	(4128)	Limit	24218	(*141*)
	4183	½	Discrete line	23899	*178*					
	4197	½	,,	23819	*258*			Structure uncertain		
	4206*	1	Sharp line	23769	..					
	4230		Limit	23634	*443*		(4080)	Limit	24503	(*426*)
II	4246	5	Very sharp edge	23545	*532*	II	4062	Very sharp edge	24611	*533*
	..	..	..	..	..	..	4057	Broad line	24642	*565*
	4273	8	High intensity edge	23396	*681*		4038	Rise of intensity	24758	*681*
	..	..	..	..	..		4032	Broad line	24794	*717*
	4292	9	Sharp edge	23293	*784*		4021	Sharp edge	24862	*785*
II*a*	4304	1	Diffuse line	23228	*849*	II*a*	4011	Diffuse line	24924	*847*
	(4323)	½	Discrete line	23126	(*951*)		(3997)	,,	25012	(*935*)
	4334	3	,,	23067	*1010*		3984	Discrete line	25093	*1016*
	4349	3	,,	22987	*1090*		3973	,,	25163	*1086*
III	4357	6	Edge	22945	*1132*	III	3966	Edge	25207	*1130*
	4360	8	Line	22929	*1148*		3963	Line	25226	*1149*
	4380	8	,,	22825	*1252*		3948	Edge	25322	*1245*
	..		..	..			3942	Line	25360	*1283*
	4395	9	,,	22747	*1330*		3935	,,	25406	*1329*
	4397	..	Sharp edge	22736	*1341*		3933	Sharp edge	25419	*1342*
iii	4406		Fairly sharp limit	22690	*1387*	iii	3927	Limit	25457	*1380*
	(4461)	1	Limit	22410	*1667*		..	..	..	..
IV	(4490)	4	Limit approximate	22265	(*1812*)	IV	(3865)	Approximate limit	25865	(*1788*)
	(4511)		Peak approximate	22162	(*1915*)		(3850)	Approximate peak	25967	(*1890*)
	(4547)		Limit approximate	21986	(*2091*)		(3827)	Approximate limit	26123	(*2046*)
V	(4611)	2	Approximate limit	21681	(2396)					
	(4635)		Approximate peak	21569	(2508)	V	(3758)	Approximate peak	26602	(*2525*)
	(4667)		Approximate limit	21421	(2656)					

* Electronic frequencies

finer details of the individual bands are taken into account. The measurements are given in Table I, along with the fluorescence results. Fig. 1*b* shows the complete absorption spectrum and in Fig. 2 is given an enlargement on a corresponding scale, showing the structure of the spectrum side by side with fluorescence.

A new detail which has been noticed regarding the principal band at 4152 in absorption, is a fine weak line splitting the band into two. This could be recorded only with difficulty, and in fact a satisfactory picture was obtained only by the expedient of using two plates edge to edge giving an absorption thickness of as much as 20 mm.

The next region ii with limits between 4128 and 4081 was too faint to be recorded with sufficient depth to enable the vague discrete structure in this region to be recorded clearly.

In the next strong band II, however, the absorption pictures taken with a suitable thickness reveal more detail. In between sharp edges at 4062 and 4021, there appear two broad lines at 4057 and 4032 with a rise of intensity at 4038.

In the region II*a*, where four discrete lines were found in fluorescence, in absorption also four distinct lines are found at 4011, 3997, 3984 and 3973. The 3997 line is very weak but 3984 and 3972 can be seen clearly even in the reproductions.

The III band was very clearly resolved by a 10 mm. thickness of a fluorescent crystal. Here again more detail was observable, showing 3 lines at 3963, 3942 and 3935 with a sharp edge between at 3948. The limits of this group are 3966 and 3933.

The remaining bands are very diffuse and without structure and the approximate limits are indicated in the Table.

It should be mentioned at this stage that in spite of the advance made, the resolution of the spectrum that has been achieved in the present work, is not all that could be desired in this direction. The principal band has considerable breadth even at liquid air temperature, and all the subsidiary bands therefore lack the sharpness necessary to resolve the bands fully. A lowering of the temperature by 22° did show a noticeable improvement in the sharpness, but experimental difficulties prevented a wider survey at this temperature. Investigations at liquid hydrogen temperature might be expected to show up the full details of the individual bands.

A second point to which attention is drawn, relates to the difference in the photographic record of the same band in emission and absorption. A very faint region stands a better chance of coming out clearly on the plate in emission, where the details stand on a clear background, while in absorption the details cease to be visible, appearing as it does as a slight fall of intensity on a dark background on the plate. On the other hand, in regions of high intensity, the contrast between closely spaced details can be enhanced and brought out clearly in absorption, by using the maximum possible thickness. The observation of a fine splitting of the principal band in absorption is a relevant example. This point is of significance when comparing the results obtained in fluorescence and absorption, as is done in the next section.

5. *Discussion of Results*

In the end-columns under absorption and fluorescence in Table I are given the frequency differences from the principal band at 4152 A. A perusal of the figures and the description in the Table brings out two significant results. The first is the presence of numerous discrete lines in the spectra with frequency shifts varying from 178 to 1330. The second important fact is the exactness of the mirror-image symmetry with respect to the 4152 band, of the details in fluorescence and absorption, in frequency shifts as well as intensities. Attention may be drawn to the figures in the Table to show how exactly the edges and other prominences are reproduced in both spectra within 5 wave-numbers, which is also the order of accuracy of the measurements for the well-defined features. As has been pointed out in the previous section, the additional details found in absorption are believed to be merely due to conditions being more favourable for observation.

The scheme of energy levels by which a symmetry pattern of this type is obtained in fluorescence and absorption has been given by the author in Part III (p. 13) of the earlier work. The scheme outlined there, assumes that the principal electronic frequency at 4152 excites vibrational frequencies and combines with them in absorption and emission. In case we are dealing with the vibration frequencies of the fluorescent centres, these may be expected to be lower, when in the excited state after absorption. The exactness of the mirror image symmetry implies that the vibration frequencies with which the electronic frequency combine in both emission and absorption are identical. In consequence, it is clear that the vibration frequencies concerned are those of the ground lattice, and the spectrum that is exhibited in fluorescence and absorption is actually the lattice spectrum of diamond.

6. *Derivation of Lattice Frequencies*

The results of the fluorescence and absorption frequencies can therefore be used to derive the full lattice spectrum of diamond. The results combining both giving mean values of the measurements are given in Table II with data available from other sources like Raman effect and infra-red measurements.

In discussing the lattice frequencies it is best to start with the well-known frequency of 1332* which appears with exceptional intensity in the Raman effect. A frequency of 1330 ± 5 appears in both spectra with considerable intensity. As has been mentioned before, this line, making due allownance for a breadth of 10 cm.$^{-1}$ on either side, gives the extreme sharpness to the edge at 4397 A in fluorescence and 3933 A in absorption. In fact, this shows that in deriving the lattice spectrum from the present data, not only the discrete frequencies which can be resolved are to be taken into account, but also the sharp edges as representing frequencies close to the measured values of the edges, within about 10 wave-numbers.

Proceeding from the 1330 frequency towards lower frequencies in the Table it can be seen that there are four discrete frequencies in this region at 1283, 1248, 1149. The edge at 1131 is too far separated from 1149 to be due to this frequency, and is therefore presumably a distinct one.

The next group consists of four comparatively weak but well separated frequencies at 1088, 1013, 943 and 848.

The region of still lower value consists of a group between 784 and 681 of high intensity and a group between 681 and 533 of lower intensity. In addition, between these limits there are resolved lines at 565 and 717. The sharpness of the edges here suggests that there are at least five distinct frequencies in this region at 784, 717, 681, 565 and 533.

TABLE II

Lattice Frequencies

Flourescence and absorption	Infra-red	Flourescence and absorption	Infra-red	Raman Effect	Flourescence and absorption	Infra-red	Raman Effect
137 (limit)		848 (line)			1383 (limit)	1372	1382
178 (line)		943 (line)					1431
258 (line)		1013 (line)					1480
443 (limit)		1088 (line)			1670 (limit)		1585
533 (limit)		1131 (limit)					
565 (line)		1149 (line)		1158	1800 (limit)	2005	
					2090 (limit)	2092	
681 (edge)			1208				
		1248 (line)	1247 (dip.)			2175	
717 (line)	710						
784 (limit)		1283 (line)	1289	1288	2400 (limit)	2481	
		1330 (line)	1330 (edge)	1332	2660 (limit)		
		1342 (limit)					

---

* The figures here and in subsequent pages refer to wave-numbers.

The lowest frequencies are of very small intensity and consist of a group of frequencies between 137 and 443. The edge at 443 is well-defined, and there are two separate frequencies at 178 and 258. These four therefore represent the important frequencies in this region.

The diffuse bands without structure, of frequencies higher than 1330 are dealt with later, as they lack the precision of measurement associated with the region of frequencies discussed so far.

7. *Agreement with Raman Effect and Infra-red Data*

As is well-known, a line of frequency 1332 cm.$^{-1}$ of extraordinary intensity has been recorded by several observers in the Raman spectrum of diamond. However, it should be pointed out that with a crystal of favourable dimensions, Bhagavantam (1930) was able to find six other faint lines with frequency shifts at 1158, 1288, 1382, 1431, 1480 and 1585, the one at 1158 being the strongest of these. It is open to doubt whether even this represents the complete Raman spectrum of diamond, as the difficulties of recording very faint lines with small crystals, which are fluorescent in addition, are only too familiar.

It will be noticed from the Table that the frequencies 1149 and 1283 from the present data agree with the frequencies 1158 and 1288 in light scattering within experimental error. Likewise, the region of faint frequencies between 1383 and about 1670 accommodates the other frequencies in light-scattering between 1382 to 1585.

Infra-red measurements also reveal a number of absorption frequencies in diamond. The available information in this field has been surveyed in an earlier paper and the approximate correspondence of the frequencies with the fluorescence and absorption frequencies shown in the form of a chart (III, p. 12). In view of the greater detail available, it is worthwhile examining the features of the curves obtained by Robertson, Fox and Martin more closely.

According to Robertson and others, there is strong absorption in the $8\,\mu$ region only in the common type of diamonds, while this is absent in the rare type. However, in the rare type which was the one investigated earlier by Reinkober (1911) there are small peaks in the absorption curve at approximately 1235, 1330, 1387, 1450, 1516 and 1600 which, as pointed out by Bhagavantam, correspond to the faint frequencies found in Raman Effect. The diamonds dealt with in the present paper were of the common type as found by ultra-violet absorption, and have therefore strong absorption in the infra-red at $8\,\mu$. The contour of the absorption curve given by Robertson *et al.* (p. 482) shows a maximum at 1208 which is not found in the present work or in light scattering. The second peak at 1289, is the same as 1288 found in Raman effect and 1283 found in the present work. A remarkable feature of the absorption curve at 8 μ given by Robertson *et al.* is the steep edge of the curve which coincides with the frequency 1332. A sharply defined dip in the curve at 1247 similarly coincides with the edge at 1248 found in the present work.

No frequencies in the region corresponding to 533 to 784 have been observed by the above authors in infra-red. But, Reinkober's earlier work gives a peak of small intensity at 710 which agrees with the broad line found in absorption at 717.

The faint band from 1383 extending to somewhat uncertain limits of about 1660 corresponds to the infra-red frequency of 1372 and the four Raman frequencies in this region. The next band of frequency between 1800–2090 with a peak at about 1900 is due to the same infra-red frequencies at 2005 and 2092. The infra-red frequency of 2175 does not appear prominently, but the next higher frequency at 2481 has a corresponding band with the approximate peak at 2500.

It has already been remarked that these higher frequency bands are very diffuse and without any noticeable discrete structure. In this connection it may be pointed out that the infra-red curves reproduced in Robertson's paper also show a similar feature. The features of the 8 μ band are sharp and stand out clearly, while the bands of lower wavelength are broader and more diffuse in their peaks. The probable reason for this is the overlapping of combinations and overtones of the lattice frequencies as will be discussed in the next section.

8. *The Complete Vibration Spectrum of the Diamond Lattice*

The discussion in section 5 was directed to the evidence that the exactness of the mirror-image symmetry implied that the fluorescence and absorption spectrum appearing in combination with the 4152 band, actually revealed the lattice spectrum of diamond. The fact that practically all the known frequencies from Raman effect and infra-red data appear also with reasonable agreement in the spectrum derived in the present work, confirms the above view, and makes it evident that there are many more frequencies present in diamond than hitherto supposed. The full spectrum therefor consists for the most part of numerous discrete lines, or in other words, monochromatic frequencies, which may be classified in broad groups between 137 to 443, 533 to 784, 848 to 1088 and 1131 to 1342.

By their very appearance, the higher frequencies than 1332 appear to be due to the presence of various combinations and overtones of the lattice frequencies proper. The overtones of the strong group between 681, 717 and 784, namely 1362, 1434 and 1568, may be responsible for the frequencies appearing in light scattering at 1382, 1431 and 1585, and in the present work as a weak band between 1383 to about 1600. Similarly the overtones of the next strong group between 1149 to 1332 is covered by the broad band between 2400 to 2660. The presence of various combinations, and the overlapping of frequencies are probably responsible for the lack of resolution of these bands. While it is possible to find suitable combinations from the lattice frequencies to explain all the higher frequencies, this can only be done with reserve, in view of the indefiniteness of the experimental values and the lack of knowledge of the selection rules.

The vibrations of the diamond lattice have been the subject of theoretical calculations by Nagendra Nath (1934). He considered a very simple type of oscillation in which the two interpenetrating Bravais lattices of carbon atoms oscillate against each other, and showed that such an oscillation should give rise to a single Raman active frequency of value about 1332. Venkatarayudu (1938) later came to the same conclusion on the basis of an analysis by group theory methods. The appearance of an exceptionally strong line in Raman effect at 1332 may be taken to mean that this picture represents approximately the most important oscillation. But the data from various sources outlined here show that many more frequencies are involved in the complete spectrum.

The extreme faintness of all the lines except 1332 in Raman effect suggests that these frequencies are either intrinsically weak, or that they are normally forbidden in Raman effect, and make their appearance due to some undetermined reasons. Likewise, the dependence of the 8 μ group of frequencies on the type of diamond, suggests that these are normally inactive and appear in infra-red absorption for similar reasons. In fluorescence and the related absorption however, all frequencies seem to be allowed to appear by selection rules and the complete spectrum reveals itself as a large number of monochromatic frequencies in addition to 1332.

The consequences of these results on the thermal properties of diamond are now examined in the following section.

9. *The Vibration Spectrum in Relation to Thermal Properties*

The lattice spectrum as shown in this work consists of a number of discrete frequencies of values ranging from 178 to 1332 of varying intensities, and not a continuous spectrum of the type conceived of by Debye and Born.

The specific heat therefore should be expressible as a sum of Einstein terms of these frequencies, with a proper distribution of weights. The question of thermal energies of solids has recently been discussed in a number of papers in these *Proceedings* (1941), of which special attention is drawn to a paper by Anand on diamond. This author has chosen some representative frequencies from the spectroscopic information detailed in this paper, and carried out the calculation of specific heat of diamond as a sum of Einstein terms due to frequencies 1332, 784, 533, 258 and 178. The basis for the choice of the frequencies, and the number of degrees of freedom allowed to each vibration, have been discussed in detail by him. The agreement that is obtained between the calculated and observed values for the entire range of temperatures, is better than that obtained by the earlier calculations on the basis of the Debye theory. His results show that next to 1332, the 784 frequency gives the most important contribution to the specific heat.

From an experimental determination of the change of the 1332 frequency with temperature, the author (IV) had on a previous occasion made an attempt to calculate the thermal expansion of diamond. Though the right order of the expansion value was obtained, the agreement was poor when compared with the actual experimental values. It was pointed out then that, the discrepancy was due to making use of the whole specific heat value for the 1332 oscillation, and ignoring the contribution due to other oscillations, at that time believed to be the Debye acoustic oscillations. The position has become clearer now, as the lack of agreement can be attributed to the failure to take into account the 784 oscillation and still lower frequencies. The variation of these frequencies with temperature, which is a necessary term in the formula for the calculation, cannot be obtained with precision from the present experiments, and so an exact calculation is not possible at present.

10. Observations on Absorption in the Ultra-Violet

As has been mentioned in the introduction, the existence of several narrow absorption lines in the common type of diamonds, was first pointed out by Robertson, Fox and Martin. They observed at room temperature 6 lines between 3290 A and 3034 A and 2 more at liquid air temperature. In the previous paper (III) the present author was able to show that lines were present up to 3450 on the long wavelength side, and on the short wavelength side they could be observed up to about 2700. In all, 15 frequencies were found and some indications of fainter lines between the strong lines. Liquid air cooling of the crystal makes these lines stronger and sharper, and in the present work the entire investigation of this region was carried out at liquid air temperature, using a spectrograph of high dispersion to record the spectrum. The experimental arrangements have been described already.

The general absorption increases very rapidly from 3450 towards the ultra-violet. Because of this factor, only limited regions can be explored at a time using a particular thickness of crystal, as details of the longer wavelength region is lost by strong transmission of light, and the shorter wavelengths by intense absorption. Pictures were obtained with various thicknesses ranging from 10 mm. to 0·5 mm., with a gradation of exposures in each case, and a selection of contact prints is reproduced in Fig. 3. The prints are arranged in exact register one below the other, as can be seen from the iron arc reference lines, showing the appearance of the spectra as the absorbing layer is decreased in depth. The first picture of the top with 10 mm. thickness shows the details of the spectrum between 3447 and 3299 very clearly, while due to strong absorption the wavelengths beyond 3202 are not distinct. This region is brought out in a series of pictures below the first. The last picture is with a thickness of 0·5 mm. and even with such a thin crystal, the further lines were found difficult to bring out with reasonable exposures.

The photographs show that between 3447 and 3015 alone, where 8 frequencies were observed by Robertson, and 10 previously by the present author, the use of suitable technique has brought out as many as 25 distinct lines. These include the lines observed by Robertson *et al.* with the exception of a line at 3242. The region between 2975 and 2715 where five more lines had been found previously could not be investigated with the same thoroughness due to experimental difficulties, but the indications are that here also, many more lines are present.

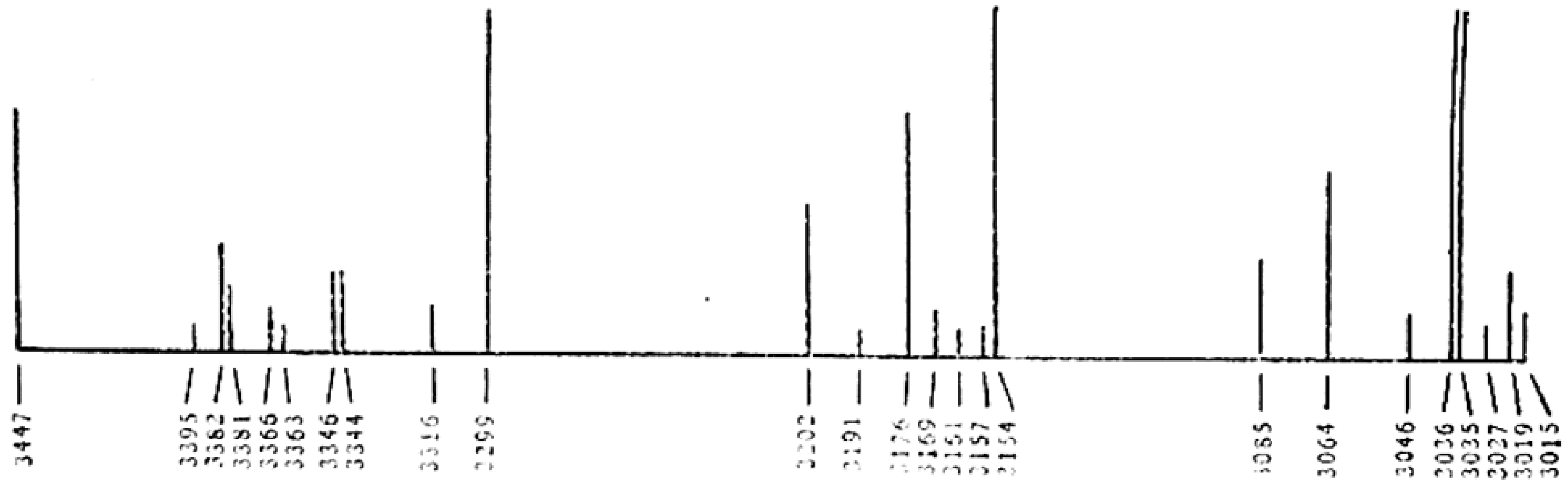

FIG. 4. The ultra-violet absorption spectrum

The wavelengths and frequencies are given in Table III. A diagrammatic representation is given in Fig. 4 on a wave-number scale with the intensities approximately indicated by the heights of the lines. Because of the rapidly altering general absorption, it is not possible to give an accurate estimate of the intensities in the entire spectrum. What has been done is to represent the relative intensities of lines within each region separately, from negatives showing all the lines in that region. For this purpose the group of lines between 3447 to 3299 is treated as one region, that between 3202 to 3154 as another group and 3085 to 3015 as still another. The relative intensities between the different groups are therefore uncertain. However, making some allowance for the increase in the general absorption, and the fall of intensity in the source of light as we go further in the ultra-violet, the diagram gives a more or less correct representation of the spectrum.

TABLE III

Absorption Frequencies in the Ultra-Violet

Wave-length	Wave-number	Wave-length	Wave-number	Wave-length	Wave-number	Wave-length	Wave-number
3447	29002	3202	31221	3085	32406	2991* to	33424
3395	29447	3191	31329	3064	32628	2976	33592
3382	29559	3176	31477	3046	32820	2958 to	33797
3381	29569	3169	31547	3036	32929	2953	33854
3366	29700	3161	31626	3035	32939	2933	34085
3363	29727	3157	31667	3027	33026		
3346	29878	3154	31697	3019	33114		
3344	29896			3015	33158		
3316	30148						
3299	30304						

* Region beyond this is not well resolved.

II. The Electronic Spectrum of Diamond

The absorption band at 4156 A and in the neighbouring region differs from the spectrum described just now in important respects. The former is directly related to the fluorescence in their intensity in different crystals. The present bands occur with practically the same intensity in different specimens, except that the factor responsible for fluorescence has a tendency to cause a slight loss of sharpness in these lines. These bands have therefore been ascribed to transitions associated with the electronic structure of the diamond lattice, as distinguished from the centres responsible for fluorescence and the related absorption.

The different lines fall into groups between 3447 to 3299, 3202 to 3154, 3085 to 3015 and a further unresolved group beyond 2900. The appearance of the last three groups resemble the bands observed in molecular spectra, with a crowding of frequencies towards the high frequency side. The lines between 3447 to 3299 do not show this feature, being separated from each other.

The behaviour of these frequencies with temperature is given in Table IV.

TABLE IV

Temperature Variation of Frequencies

Line	4152		3447		3299		3154		Raman line	
Temp. °K										
85°	24077	·83	28999	·83	30303	1·5	31699	1·6	1333·8	1·3
300°	24057		28975		30257		31648		1332·1	

The change of the frequencies between 85° and 300° is shown in each case as a shift per 1000 wave-numbers. The changes are all of the same order, and nearly the same as the change of the lattice frequency found in the Raman effect. The 4152 fluorescence line and the 3447 line have the same change which is lower than that of the lattice frequency. The lines 3299 and 3154 have nearly double this value, but it should be mentioned that there is some uncertainty in the measurement because of the broadening of the lines at 300.° In a few cases where data at CO_2 temperature were available, it was observed that between 85° and 195°, the change was small compared with the change between 195° and 300°. The fact that all these changes are of the same order of magnitude suggests that the binding electrons in the lattice are responsible for the lines, and it is significant that they are affected in the same way as the lattice frequency is affected by temperature.

The electronic structure of diamond worked out theoretically by Kimball was referred in the previous work. Here the energy levels corresponding to the $2s$ and $2p$ levels of carbon are conceived of as broad bands when they form the diamond structure. Kimball's results do not show the possibility of absorption anywhere in the region described in this paper. The fact that the lines are extremely sharp suggests sharply defined electronic levels rather than the broad bands arrived at on theoretical grounds. The basis of this calculation deserves further examination.

12. *Absorption Lines in the Visible Region*

Absorption lines in the long wavelength side of 4152 were looked for without success before. By the use of 2 crystals put edge to edge and increase of effective thickness, four more absorptions have been found in this region. The first is a very sharp line at 4206. This coincides exactly with a fluorescence line in this region and is an electronic frequency of the same character as, but of negligible intensity compared with the 4152 band.

A broad band at 4770 is interesting as previously such an absorption was found only in yellow crystals and was considered unusual. Evidently this absorption differs in intensity in different crystals. In the author's paper on phosphoresence (II—page 540) it was shown that the part of the spectrum which occurs as phosphorescence in the long wavelength region is excited with special intensity when the exciting radiation is about 4700. The absorption band here is therefore of particular interest. Two very sharp lines were also observed at 4958 and 5034. These new lines, it should be remembered, are recorded only with a great thickness, and are therefore very weak and of subsidiary importance.

In conclusion, the author's grateful thanks are due to Professor Sir C. V. Raman for his helpful interest and encouragement in this work.

13. *Summary*

The fluorescence and absorption spectra of diamond show a perfect mirror image symmetry about the sharp electronic band at 4152 A. They split up into discrete lines at liquid air temperature. From the observed frequency differences are derived the following wavenumbers for the fundamental vibrations of the dimaond lattice: *1330*, *1283*, *1248*, *1149*, *1131*, 1088, 1013, 943, 848, *784*, *717*, *681*, *565*, *533*, 433, 258, 178 and 137, those in italics being the strongest. The discrete character of the lattice spectrum thus indicated is inconsistent with the idea that the atomic oscillations in a simple crystalline solid are of the same physical nature as the vibrations of an elastic solid.

In addition to the 4152 A line which was found to be a close doublet in absorption, more than 25 discrete frequencies have been listed in the ultra-violet spectrum beyond 3447 A. The strongest absorptions were at 3447, 3299, 3202, 3176, 3154, 3036 and 3035 with fainter lines between these, and an unresolved group beyond 3000 A. The change of the absorption frequencies with temperature is of the same order of magnitude relative to the absolute frequency, as the change of the 1332 lattice frequency with temperature. The experimental results generally indicate that the absorption frequencies in the ultra-violet as also a few additional weak lines appearing in the visible region, should be ascribed to the transitions between the electronic energy levels of the diamond structure.

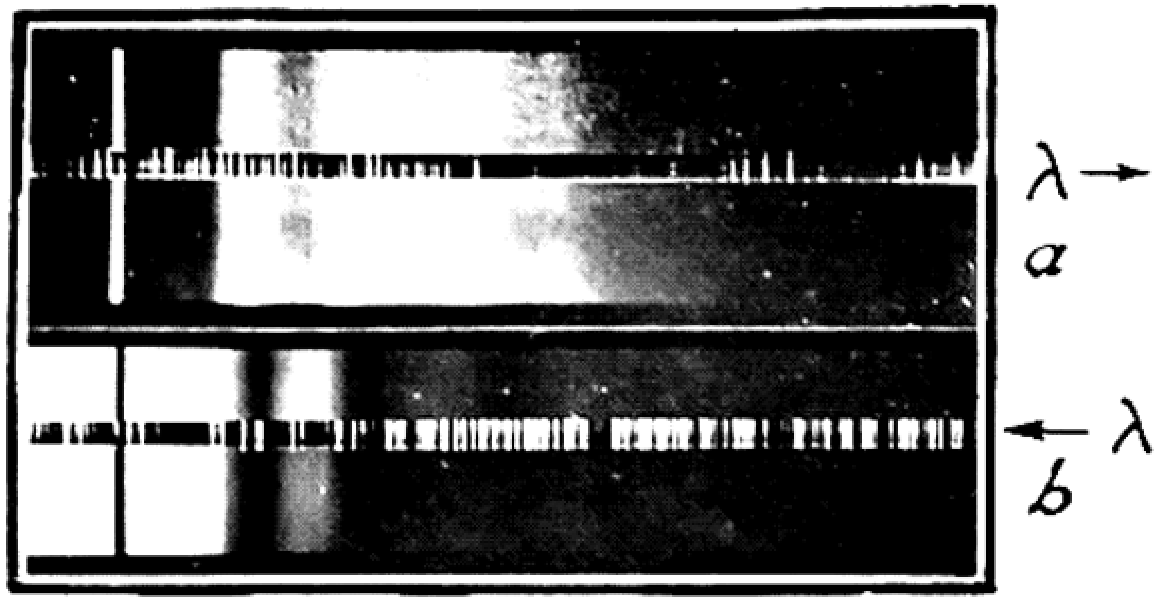

FIG. 1 (*a*) Fluorescence between 4150 Å and 4900 Å, and (*b*) absorption between 4150 Å and 3600 Å

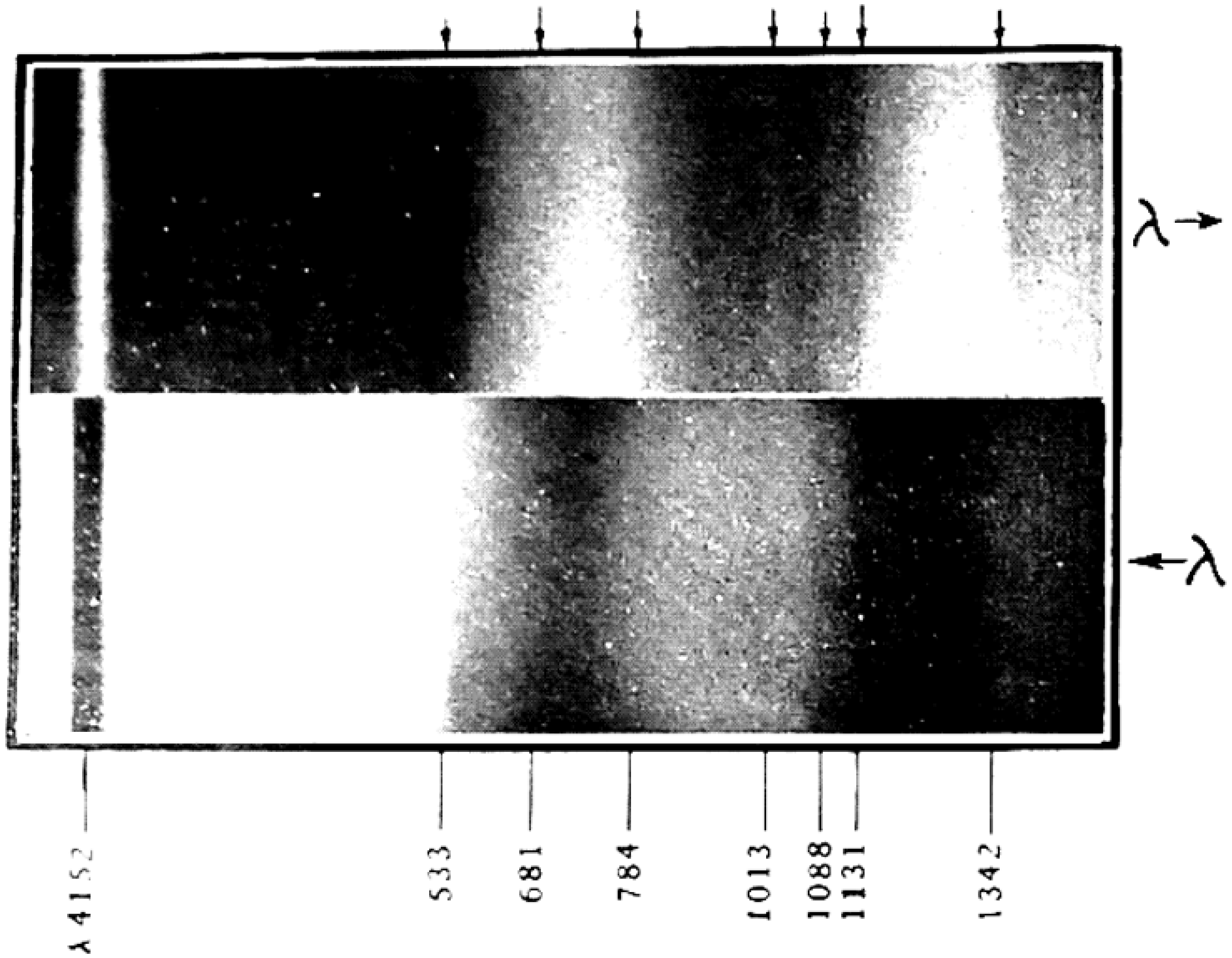

FIG. 2. Part of Fig. 1 enlarged showing frequency shifts of principal features

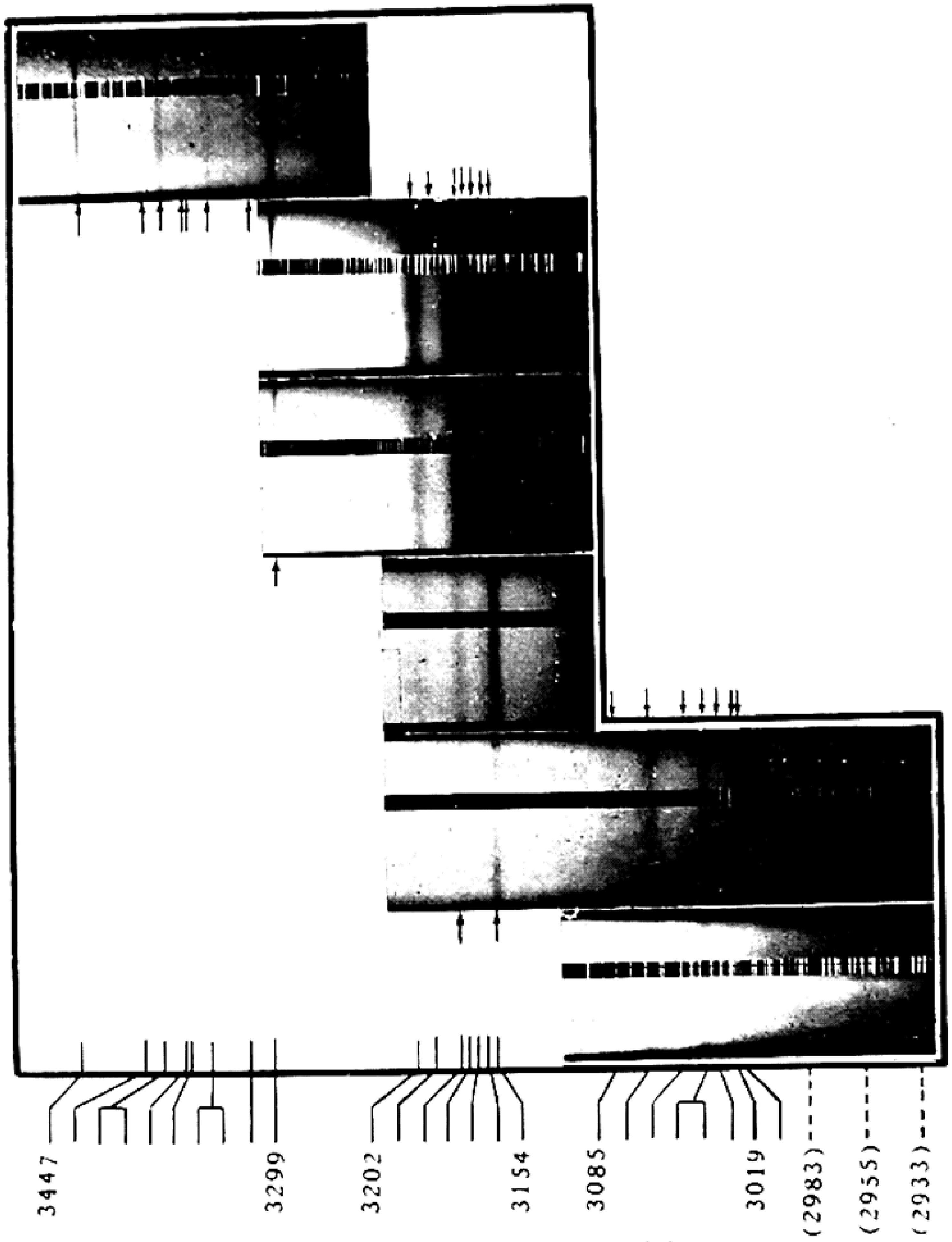

FIG. 3. Absorption bands in ultra-violet

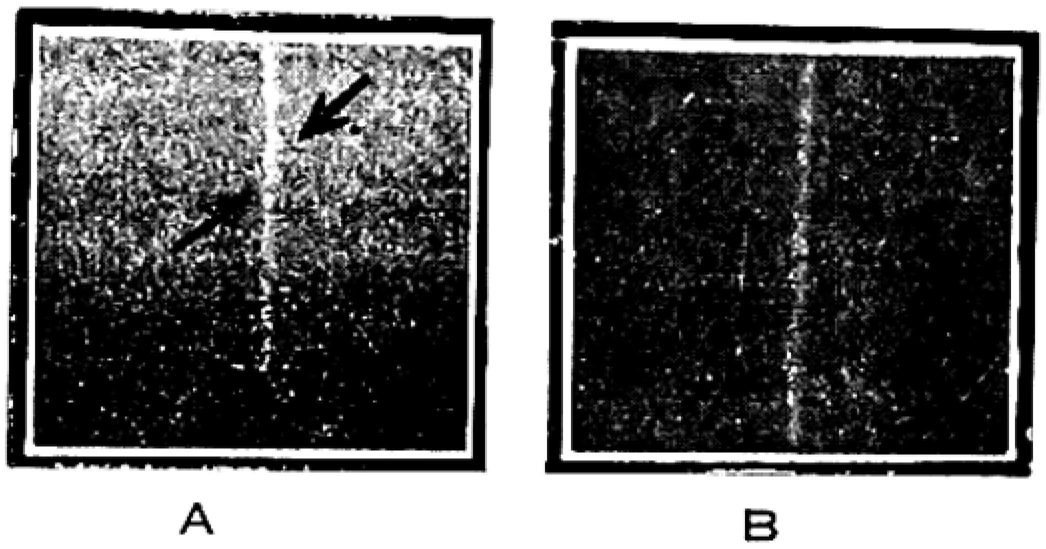

FIG. 1. Enlargement of 1332 line showing irregularity in an imperfect diamond (A) in comparison with the line in a normal diamond (B)

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* ERRATA.—In these papers the following misprints occurred: I, table II, *for* 4256 *read* 4156; III, table II, *for* 1200 *read* 1900.

THE LUMINESCENCE, ABSORPTION AND SCATTERING OF LIGHT IN DIAMONDS: PART IV. RAMAN EFFECT

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1. *Introduction*

The Raman spectrum of diamond is a subject which has already received a good deal of attention. The line of exceptional intensity which appears with a frequency shift of 1332 cm.$^{-1}$ was first reported as early as 1930 by Ramaswamy, and also about the same time by Robertson and Fox (1930). Bhagavantam recorded the spectra of a large number of diamonds including some of fairly large size, and found six additional lines of extremely feeble intensity. Robertson, Fox and Martin (1934) found that the frequency shift of 1332 was the same in the two types of diamonds recognised by them, in spite of the remarkable differences in their infra-red and ultra-violet absorption spectra. The modes of oscillation of the diamond lattice have been worked out theoretically by Nagendra Nath (1934) and Venkatarayudu (1938) who agree in identifying the 1332 frequency as arising out of the oscillation of the two interpenetrating Bravais lattices of carbon atoms. In a paper which has appeared in these *Proceedings* (1941), the present author dealt with the alteration of this frequency with temperature and its relation to the thermal behaviour of the crystal.

The author has had occasion to study the scattering of light in a number of diamonds during the course of an extended investigation of their luminescence spectra. The present paper records certain observations made on the intensity, frequency and polarisation of the 1332 line in different crystals.

2. *Nature of the* 1332 *Lattice Oscillation*

The scattering of light in crystals with change of frequency cannot, as in the case of gases or liquids, be considered as arising from the vibrations of independent ionic or molecular units. This is obvious since a crystal is a coherent mechanical structure and the vibrations extending through the entire irradiated volume have therefore to be taken into account. The force of this remark is particularly evident in the case of diamond where the entire crystal is an extended structure of carbon atoms bound together by valence forces and forming a " giant molecule ". If the atoms in all the lattice cells vibrate in the same phase, the crystal as a whole would still be optically homogeneous and would not, therefore scatter any light. This difficulty is removed if it be assumed that the phase of the vibrations changes progressively from cell to cell in such a way that the phase-waves may be regarded as periodic stratifications of optical density. If such stratifications are of appropriate wave-length and have the appropriate inclination, they would be capable of giving a monochromatic reflection of the incident rays, the change of frequency occurring in such reflection being equal to the frequency of the lattice vibrations in the crystal. Since the wave-length of the stratifications would necessarily be of the same order as that of light and therefore large compared with the crystal spacings, the frequency of the lattice vibrations and the consequent change of frequency in scattering would be practically independent of the phase-wavelength and therefore also of the angle of scattering.

Whether the frequency of the lattice vibrations depends to any detectable extent on the phase-wavelengths operative in light scattering was tested experimentally by a comparison of the frequency shift in diamond in transverse and in nearly backward scattering of light. A spectrograph giving about 20 A/mm. dispersion in the 4300 region was employed. A difference of 1 wavenumber, if present, would have been detectable in view of the sharpness of the line which was recorded side by side for the two cases using a Hartmann diaphragm. No difference in the spectral position of the Raman lines for the different angles of scattering could be detected.

It is usual to assume that the radiations scattered within a crystal emerge in all possible directions and that for a cubic crystal the intensity would be independent both of the orientation of the crystal and of the angle of scattering, if we exclude polarisation effects. It appeared worthwhile to test experimentally whether this assumption is actually justified in the case of diamond.

Using a diamond of suitable shape having a pair of faces coincident with the octahedral planes, the intensity of the Raman line was compared for different settings of the crystal. A narrow well-defined beam was used for illumination and precautions were taken to eliminate internal reflections of light. The cases specially investigated were those in which the phase-waves within the crystal responsible for the scattering of light lay in the vicinity of the principal crystallographic planes. Thus, the crystal was illuminated normal to one octahedral face, and the scattering observed, firstly in a direction normal to the neighbouring octahedral face, and then at various angles up to 20° on either side of this. Since the octahedral faces are equally inclined to the cube face transverse to them, the phase-waves in the first case were parallel to a cube face and in the other cases inclined to it. No sensible variation of intensity was however found in these settings. Likewise, using a flat plate with its face parallel to the octahedral planes, the intensity of the Raman lines was recorded in the cases when the reflections were due to phase-waves respectively parallel to the (111) plane and inclined to it at various angles. Here again, no noticeable differences in the intensity of the 1332 Raman line were observed.

In the case of the modified reflection of X-rays from the (111) planes of diamond, the phase waves of the lattice vibrations are known to have specified orientations parallel to the cube faces (Raman and Nilakantan, 1941; Pisharoty, 1941). The position is thus different from that observed in the case of light scattering. It does not however appear to be impossible to reconcile the optical and X-ray results, since in the former case we are dealing with phase-wavelengths which are comparatively much larger, being of the order of some thousands of angstrom units, while in the X-ray case we are dealing with phase-wavelengths of the order of fifty angstroms or less. The variation of frequency of the lattice vibration with the phase-wavelength would be much more noticeable in the latter region. Hence, the phase-waves parallel to the three sets of cubic faces must be considered to be incoherent and therefore independent of each other for the X-ray reflections, while they would be coherent and capable of combining in light scattering.

3. *Polarisation of Raman Line*

The two earlier observations on the polarisation of the 1332 line are not in agreement. Ramaswamy found the line well polarised, but Bhagavantam reported that the polarisation was imperfect. The latter author however pointed out that since the cut of the diamond crystals generally met with are such as to cause repeated internal reflections, the results were not quite reliable. In the present investigation, a crystal of favourable shape and size was available and a determination of the value of depolarisation was made. This crystal had two opposite faces nearly parallel and two neighbouring faces nearly at right angles. The transversely scattered light was condensed on the spectrograph with a double image prism in the path to give two separate images one vertically and the other horizontally polarised. A further check on the experimental result was made by repeating the experiment with the crystal immersed in benzene to eliminate internal reflection of light.

The horizontal and vertical components (after allowing for instrumental correction) were of equal intensity giving the value of 1·0 for the depolarisation factor. The components of the polarisability tensor for the different classes of crystals have been tabulated by Saxena (1940). Of the possible vibrations of the cubic class, the symmetric and doubly degenerate vibrations give rise to polarised Raman lines. The 1332 line according to the present ideas comes under the triply degenerate class, and the depolarisation value theoretically obtained from the tensor components is 2. The fact that none of the three classes of oscillation possible gives the value of 1 observed in experiment is a discrepancy which awaits elucidation.

4. *Intensity and Frequency in Fluorescent Diamonds*

As has been pointed out elsewhere, the Raman line of frequency 1332 cm.$^{-1}$ in diamond can be considered to have its origin in the oscillation of the two interpenetrating cubic lattices against each other. It is a point worth consideration whether diamonds of widely differing fluorescing power would show any variation in their scattering power as well. In fact, Bhagavantam had made an observation in the course of the paper referred to already, that clear and colourless diamonds appear to show a stronger Raman line than blue (fluorescent) diamonds, in which the line appeared to be intrinsically weak.

The intensities of the Raman line in the four plate-shaped diamonds (D_1, D_2, D_3, D_4) were compared, using the same technique as was employed in comparing fluorescence intensities (Part I). The only difference was that the 4046 line of the mercury arc was suppressed with a filter of sodium nitrite solution to allow the Raman line to be registered without being masked by the fluorescence spectrum. No sensible difference in the intensities was found in spite of the fact that D_2 was roughly 100 times as intense in its fluorescence as D_1. Bhagavantam's observations was presumably due to the fact that the intense background masked the Raman line, as no difficulty was found in registering the line with the usual intensity even in the case of the specimen D_7 exhibiting very intense fluorescence, once the fluorescence was suppressed by cutting off the 4046 line.

The frequency of the line was found to be exactly the same in all the crystals except in the case of an imperfect crystal which is dealt with below.

These results are explicable if it is assumed, as has been done already, that the luminescence and related absorption effects are due to local centres which do not affect the lattice as a whole.

5. *Frequency Variations in an Imperfect Diamond*

The 1332 line is extraordinarily sharp, but among the crystals studied, it was found that in one diamond the line was not as well defined as in the others. This particular crystal was in the form of a plate with polished faces and a careful investigation was made of the peculiarity shown by the line. For a crystal of this shape, transverse scattering was not possible and so the scattering was studied in a nearly backward direction, with a filter of $NaNO_2$ solution to suppress fluorescence. A sharp image of the diamond plate was formed by a lens, filling the entire length of the spectrograph slit, so that the scattered light from different portions of the crystal corresponded to different positions on the line in the spectrum. The Raman line was found to exhibit a minute fluctuation of frequency and was slightly "wobbly" as compared with other lines. To eliminate the possibility of any local displacement of the gelatine film on the photographic plate, a number of plates were taken, all of which showed the effect. Neither could it be ascribed to any defect of the slit, as pictures of other diamonds taken without disturbing the slit showed perfectly sharp and straight lines. The experiments were repeated with another instrument (a Hilger E_2 spectrograph with better definition), and the wandering of the line was confirmed. The enlargement of the scattered line in two cases is shown side by side in Plate VIII and the slight irregularity in one case is indicated by arrows.

It is noteworthy that Bhagavantam has also reported an irregularity of the line in one of the diamonds examined by him.

The line as it appears on the plate is an image of a linear section of the crystal formed by scattered light, and there is a correspondence between points on the crystal and points on the line. It is therefore evident that the lattice is disturbed in some portions of the crystal by strains. In the study of the variation of the 1332 line with temperature, and its relation to thermal expansion, the author (1941) drew attention to the fact that a change of 3% in the volume by thermal expansion causes a change of 7% in the frequency of this line. From this and the known compressibility of diamond, an estimate may be made of the pressure required to bring about a small change of frequency of this line. The minute changes in frequency where the Raman line is irregular are of the order of 1 wave number. Calculation shows that a stress of the order of 1000 atmospheres could bring about this order of variation. It is well known that some diamonds exhibit a considerably strained condition and are even known to explode spontaneously when removed from the matrix. It appears possible that an intense local stress of the above order of magnitude is responsible for the irregularity of the line.

In conclusion, the author wishes to express his respectful thanks to Professor Sir C. V. Raman for his interest and encouragement in this work.

6. *Summary*

This paper records various observations on the frequency, intensity and polarisation of the Raman line of frequency shift 1332 cm.$^{-1}$ in diamonds. The scattering has been considered as a monochromatic reflection by phase-waves, and the consequences are discussed. No change in the frequency within 1 in 1000, nor any difference in intensity was found by varying the setting of the crystal or the angle of scattering. The depolarisation value was found to be 1, in disagreement with the supposed theoretical value of 2. The intensities and frequencies of the line in crystals varying enormously in their fluorescence and absorption properties were compared quantitatively and found to be sensibly the same. An interesting case of an irregularity of the spectral line noticed in an imperfect crystal is illustrated in the paper, and a suggestion is made that an intense local stress of the order of 1000 atmospheres is responsible for such an effect.

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INTERFEROMETRIC STUDIES OF LIGHT SCATTERING IN GASES

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Introduction

Rayleigh's theory of light-scattering in gases is based on the assumption that the molecules of the irradiated gas behave as Hertzian dipoles and emit secondary radiation in all directions. It is assumed further that these secondary radiations are incoherent with each other. The justification for the latter assumption is to be found in the fact that the molecular positions in a gas are distributed at random, and the phases of the scattered radiations as received at any point in space are therefore uncorrelated. The matter may also be considered from another standpoint. The molecules of the gas are in motion, and hence the scattered radiations suffer Doppler shifts of frequency varying from molecule to molecule and in consequence are incapable of interfering with each other. Hence, if the incident radiations consist of a sharp spectral line, the scattered radiations should exhibit a spectral broadening, the magnitude of this depending on the mass of the molecule, on the temperature of the gas, as well as on the direction of observation. It is evident that such Doppler broadening would be unobservable in the direction of the incident beam and would be a maximum in the backward direction. Such a state of affairs would subsist even in the case of highly compressed gases, so long as they continue sensibly to obey Boyle's law (C. V. Raman, 1922). It is therefore very different from what is experimentally observed in the case of dense media such as liquids where discrete Doppler-shifted components are observed in the spectrum of the scattered light, the magnitude of the shift depending on the velocity of sound in the medium and the direction of observation. The present investigation describes an interferometric study of the scattering of light in some compressed gases intended to test the theoretical considerations indicated above.

Experimental

It is obvious that the most favourable direction for the observation of the scattered light is backwards to the incident beam, as the Doppler effect is then a maximum. Further, when the observation is made in this way, the depth of the illuminated gas can be made large with a corresponding gain in intensity while retaining the desirable definiteness in the angle between the incident and scattered rays. The intensity is also greater with backward than for transverse scattering, as both components of polarisation in the incident light are effective in the former case. For the successful observation of the spectral character of light scattering, it is very important to avoid parasitic light from the walls of the tube and to maintain the interferometer at a constant temperature. Indeed, Cabannes (1929) who studied the problem using butyl alcohol vapour and transverse scattering obtained a shift of the fringes towards longer wavelength, which has since been shown by Rao (1934) to be a spurious effect due to temperature variations in the apparatus. A satisfactory experimental arrangement used by the author is illustrated in Fig. 1. The cylinder T containing the gas is made of a mild steel tube $1\frac{1}{2}''$ in internal diameter, $\frac{3}{8}''$ wall-thickness, and $1\frac{1}{2}'$ long, blackened inside by spray painting. The observation end is closed with a round glass plate W of $\frac{5}{8}''$ thickness and pressed air-tight by means of lead washers and a screw cap. The back end of the cylinder is similarly closed by another screw-cap to which is fitted a gas adapter. A satisfactory dark background is provided by a black glass plate fixed in a brass tube at 45° to the axis of the cylinder. A blackened brass tube which is water cooled and into which is fitted a series of circular apertures of $\frac{1}{4}''$ diameter, is fixed flush with the glass window. The source of light used is a semi-circular mercury arc A with water-cooled cathode and kept at high vacuum by continuous pumping. The light passes through the annular space,

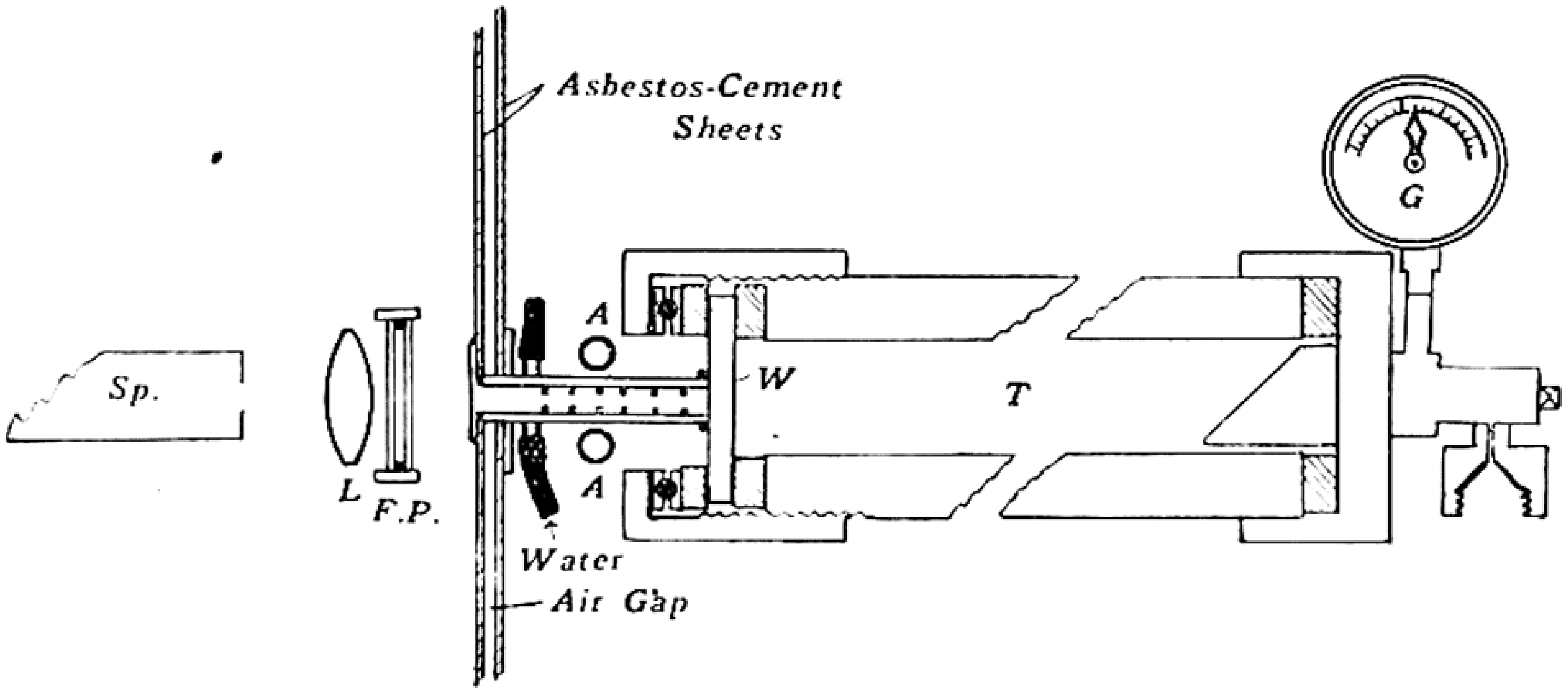


FIG. 1. The Diagram of Gas Container

about $\frac{1}{4}''$ broad, between the central brass tube and the outer screw-cap. The light scattered backwards is taken through the central tube and let fall on a quartz Fabry-Perot interferometer F. P. with invar separation pieces. The interference fringes are focussed on the slit of a Fuess glass spectrograph. The interferometer and the spectrograph are placed inside an air-tight enclosure made of asbestos-cement sheets. The whole outfit is situated in a large room with massive walls in which the temperature fluctuation is very small, and the provision of the additional enclosure for the optical system ensures constancy of temperature throughout the exposure extending over several days.

The plate-distance used for the etalon is 7·5 mm. For this separation of plates, the distance between consecutive orders is 0·66 cm.$^{-1}$, and the hyperfine structure pattern of 4046 A.U. is given in Fig. 2. It will be seen that the satellites fall either on the principal maxima or at the centre, leaving a clear gap in between.

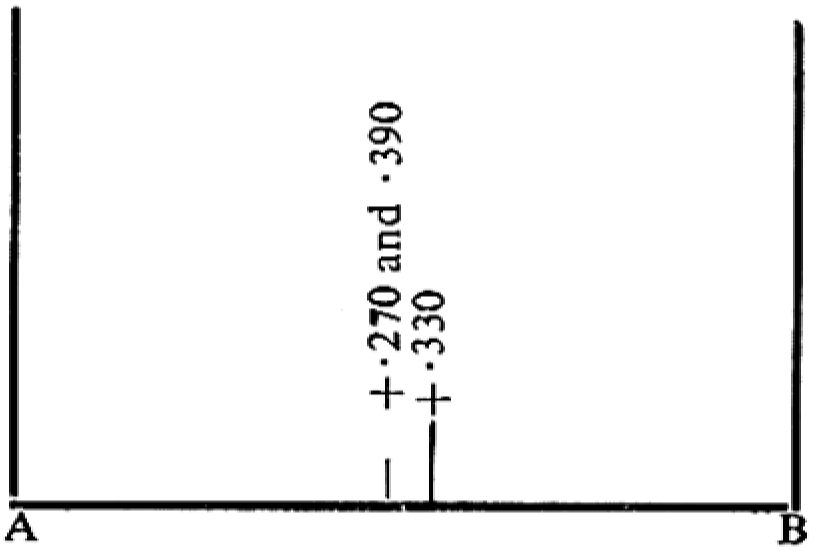


FIG. 2. Satellites of 4046 A.U. radiations

$\delta\nu_{AB} = \cdot 66$ cm.$^{-1}$

The gases used are hydrogen at 100 atmospheres, oxygen at 80 atmospheres, nitrogen at 80 atmospheres, and carbon dioxide at 50 atmospheres pressure. The gases are let into the experimental tube from commercial holders through a plug of cotton wool which filters out all dust particles. The scattering being extremely weak, nearly fifteen days exposure was required in each case.

Results and Discussion

Figures 4 *a–e* in the accompanying Plate show the interference patterns of 4047 A.U. radiations given by the arc and after it is scattered by hydrogen and nitrogen. The patterns given by oxygen and carbon dioxide are similar to those of nitrogen. In no case were shifted components analogous to those given by liquids observed. It may be recalled that the discrete line structure of the rotational Raman scattering in oxygen, nitrogen and carbon dioxide has been observed by Bhagavantam (1931), Trumpy (1933) and Weiler

(1935), to disappear at such high pressures. The absence of any Doppler-shifted component in the spectrum shows that though the mean free path of the molecules at these pressures lies between 11–16 A.U. and is thus fairly small, it is sufficiently great in comparison with the molecular dimensions to ensure the absence of any coherence between the scattering units. The interference patterns due to the heavier gases N_2, O_2 and CO_2 are very nearly identical with that of the direct arc, except for a weak continuum between the rings, which is absent in the latter. In the case of hydrogen, the rings in the pattern show considerable broadening with the intensity falling off gradually on either side. Similar broadening is also exhibited by the 4358 A.U. radiations. It is observed that in accordance with the Rayleigh's fourth power law, the green radiation of the arc is recorded only weakly in the spectrum of the scattered light, while it appears with good intensity in the spectrum of the arc. This indicates that the scattered light is fairly free from parasitic illumination. The Raman spectrum of the gas obtained after removing the interferometer also shows that stray light does not interfere with the observations.

Assuming the validity of Maxwell's law of distribution of velocities of the molecules in the systems studied, we can ascertain the spectral intensity distribution in the scattered radiation. If a molecule possesses a velocity u along the bisector of the angle θ between the incident and the scattered beams, the frequency of the incident radiation would change by Doppler effect from n_0 to $n_0\left(1 \pm \frac{2u}{c}\sin\frac{\theta}{2}\right)$, where c is the velocity of light, the positive sign corresponding to the case in which the molecule is moving towards the light and the negative sign for the molecule receding away from it.

As the velocity components of molecules in any particular direction vary from zero to a large value, the scattered light will have a range of frequencies about the central value n_0. The intensity of light scattered with a particular frequency, $n_0\left(1 \pm \frac{2u}{c}\sin\frac{\theta}{2}\right)$ corresponding to the velocity u, will depend on the number of molecules possessing that velocity, which is given by the Maxwellian distribution of velocities. The intensity I corresponding to a velocity u may accordingly be written as $I = I_0 e^{-\frac{1}{2}\frac{mu^2}{kT}}$, where I_0 is the intensity corresponding to $u = 0$, while m, k and T are respectively the mass of the molecule, the Boltzmann constant and the absolute temperature. Now the velocity corresponding to the half-breadth of the line is given by the value of u at which $\frac{I_0}{I} = 2$, namely $u = \sqrt{2 \log_e 2 \cdot \frac{kT}{m}}$ and the change of frequency corresponding to this velocity is $\delta n = \frac{2n_0}{c} \sin\frac{\theta}{2} \cdot \sqrt{2 \log_e 2 \cdot \frac{kT}{m}}$. Expressed in wavenumbers this may be written as

$$\delta \nu = 2\nu_0 . \sin\frac{\theta}{2} \sqrt{2 \log_e 2 \cdot \frac{kT}{mc^2}}.$$

At the room temperature and for the 4047 A.U., the calculated half-breadth for hydrogen comes to 0·22 cm.$^{-1}$ and for the other three gases less that 0·06 cm.$^{-1}$ Though theoretically the half-breadth for the mercury vapour at the temperature of the arc should be only 0·03 cm.$^{-1}$, the actual half-breadth of the interference maxima measured microphotometrically gives a value of 0·08 cm.$^{-1}$ It will be seen that the expected half-breadths for nitrogen, oxygen and carbon dioxide are less than this value, which explains the observed results. Fig. 3 shows the microphotometer tracings of the 4047 A.U. line scattered by hydrogen and of the direct arc. The half-breadth obtained from the above curve is 0·18 cm.$^{-1}$ which is of the same order of magnitude as the theoretical value. The background that is observed in the patterns of the scattered light and which is particularly noticeable for hydrogen may be attributed to molecules having relatively high velocities.

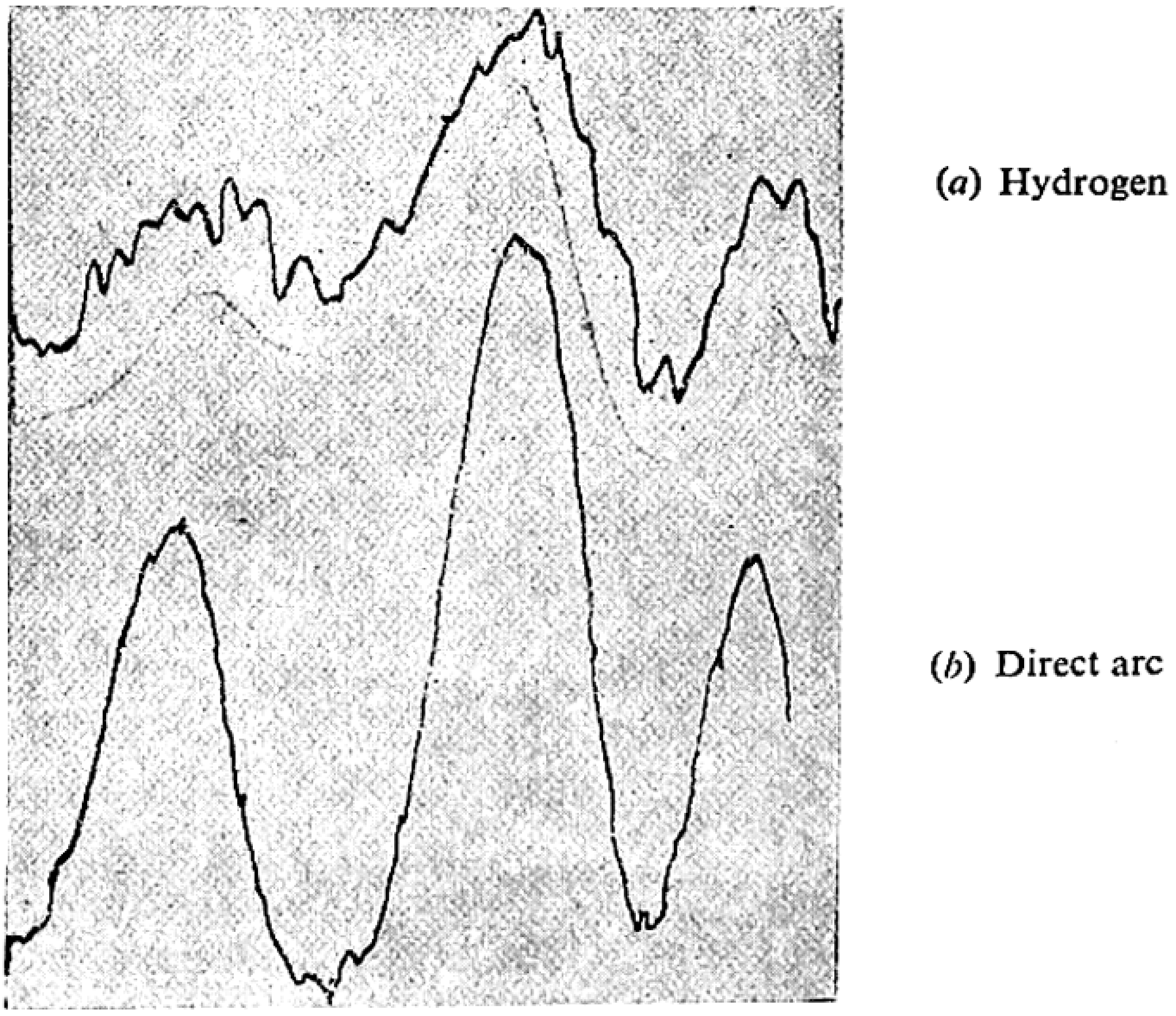
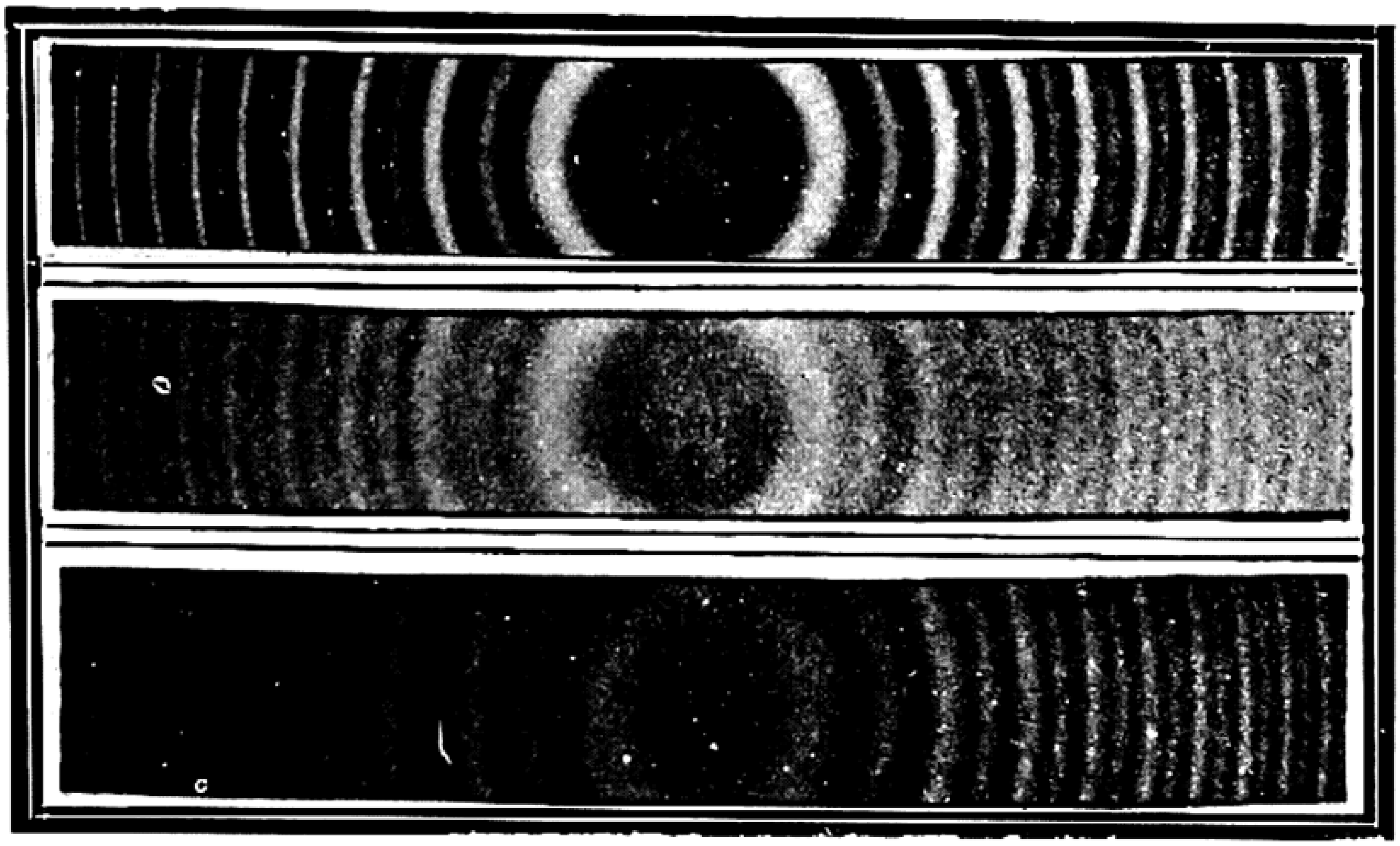


FIG. 3. Microphotometric tracings for hydrogen gas



(*a*) Direct

(*b*) Hydrog

(*c*) Nitroge

FIG. 4. Interferometer Patterns for Gases

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In conclusion, the author wishes to express his thanks to Professor Sir C. V. Raman at whose suggestion the investigation was undertaken, for his kind interest in the work.

Summary

Light scattered backwards by four gases, namely, hydrogen, nitrogen, oxygen and carbon dioxide at high pressures has been analysed by a Fabry-Perot interferometer. None of the gases showed displaced components similar to those in liquids. For the heavier gases, N_2, O_2 and CO_2, the Doppler broadening was observed to be too small to be detectable with mercury radiations. The pattern obtained for hydrogen showed a broadening and the half-breadth of the line was found to be of the order to be expected from Maxwell's law of distribution of velocities. A weak background due to molecules having relatively high velocities was observed in the scattered patterns for all cases.

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INTERFEROMETRIC STUDIES OF LIGHT SCATTERING IN MOBILE LIQUIDS

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1. *Introduction*

A description of the liquid state requires a knowledge of the distribution of molecules within the fluid, as also of their movements and their mutual interactions. Spectroscopic studies on the scattering of light afford probably the most direct method of obtaining information regarding these matters and are thus of great importance in enabling us to reach an understanding of the liquid state.

The molecular movements in liquids are of three different kinds in diminishing order of frequency, namely, the molecular vibrations, the molecular rotations which in the vast majority of liquids are hindered by collisions, and the translatory movements which are also restricted in the same way. It is with the two latter types of motion alone and especially with the last that we are here concerned. The present paper deals, in fact, with the scattering of light in dust-free liquids, occurring either without change of frequency or with frequency changes so small that they require interferometric aid for detection.

The translatory motions of the molecules in liquids would obviously give rise to Doppler shifts of frequency in the scattered light of the same nature as those observable in gases and dealt with in an earlier paper in these *Proceedings*. In the vast majority of liquids, however, such changes of frequency would, in view of the large molecular masses involved, be too small to be detectable. Considerably larger shifts falling within the range of interferometric study may, however, arise in a manner first indicated by Brillouin (1922). In the theory of the latter, the discrete molecular structure of the fluid is ignored and the scattering is regarded as a monochromatic reflection of the incident light waves by trains of sound waves of appropriate wave-length and orientation forming regular stratifications in the medium. Such reflections would be accompanied by Doppler shifts of frequency in one direction or the other and of a magnitude determined by the velocity of the sound waves in the fluid. That the effect contemplated by Brillouin does arise in liquids is now a well-established experimental result. It is evident, however, that Brillouin's theory cannot completely describe the effects observable with liquids. The discrete molecular structure and especially the random molecular orientations may be expected to give rise to phenomena of a different kind. The assumption that the thermal agitation takes the form of extended wave-trains propagated in a regular way may also depart from the truth in certain circumstances, *e.g.*, in highly viscous liquids and even in mobile liquids at high temperatures. A point of view which embraces Brillouin's theory but which is sufficiently general to include all such possibilities is to regard the changes of frequency in every case as a Raman effect. The translatory movements of the molecules would evidently produce local fluctuations of optical density in the medium. These would, in general, vary with time and the resultant scattering should accordingly exhibit frequency changes which are both positive and negative. Variations of optical density which are of a quasi-static or stationary character, if present, would give a scattering of unaltered frequency. On the other hand, pulsations of optical density taking place over an extended domain in the fluid and travelling through the medium in the manner of sound waves would give a coherent modified scattering, the resultant effect being spectral shifts varying with the direction of observation in the manner indicated by the Brillouin theory. The interferometric study of light scattering thus, in effect, enables us to make a frequency analysis of the fluctuations of optical density and to find whether they occur with or without correlation of phase at different points within the fluid (Raman and Venkateswaran, 1938).

2. *Experimental Arrangements*

A : Choice of Interferometer.—Among the previous investigators who have worked on the present subject, Gross (1930), Meyer and Ramm (1932), Ramm (1934) and Birus (1937) have used an echelon grating, while Rafalowski (1931) has used the Lummer-Gehrcke plate; but the most satisfactory patterns have been obtained with a Fabry-Perot etalon by Rao (1934). The author has examined the efficiency of various interferometers in order to choose the instrument best suited to the problem. For this purpose the 4047 A.U. radiation of a mercury arc scattered by ethyl alcohol was examined by (1) a 36-step reflection echelon having pressure and temperature controls supplied by Adam Hilger and Co., (2) a Lummer plate of glass of length 130 mm. and thickness 4·48 mm. and (3) a Fabry-Perot etalon of quartz with invar separation specially made by Heinrich Lesche of Potsdam. It was observed that the etalon gives the maximum separation and definition of the fine structure components though with a low intensity, while the Lummer plate gives the maximum intensity but with the disadvantage that the fringes are somewhat broad. The echelon is unsuited for these investigations in spite of its high resolving power, on account of its low luminosity and dispersion and the complicated nature of the interference pattern. In the following investigations, the etalon has been used for recording the fine structure components and the Lummer plate for polarisation studies in which the intensity of scattered light is necessarily low.

B: The Source.—In most of the previous investigations, the 4046 and 4358 A.U. radiations of a high vacuum mercury arc were used for the incident light. These lines suffer from the disadvantage that they are accompanied by intense hyperfine structure satellites which make their appearance in the scattered light. 4358 A.U. is particularly unsuited as the principal maxima themselves are excessively broad. 4078 A. U. is comparatively more satisfactory, as the hyperfine structure components are of relatively low intensity. These features of the mercury radiations are illustrated in Fig. 5, Pl. X. For the purpose of getting reliable data, it is of the utmost importance to use highly monochromatic and sufficiently intense radiation. The blue triplet, 4680, 4722 and 4810 A.U. of the zinc arc satisfies these requirements.* As however, a pure zinc arc requires a high current density for continuous running, these lines become broad and undergo self-reversal. Therefore, a zinc-mercury amalgam arc in pyrex glass was developed in the course of the investigation here described. The amalgam contains 12–15% by weight of zinc and the arc is run at a current of about 4 amps. The blue triplet is then sharp and moderately intense and nearly as efficient as 4078 A.U. for scattering and gives a structureless interference pattern with fairly sharp maxima (Fig. 6, Pl. X). For studying the longitudinal scattering of light, the arc is made in a semicircular form.

C: The Choice of Scattering Direction.—The previous authors have observed the scattered light in a direction either at right angles to the incident beam or at an angle of 180° to the latter. While the transverse direction has the advantage that a perfect background free from any back reflection could be provided for scattered radiations, it suffers from the drawback that the magnitude of the Brillouin shift is only $1/\sqrt{2}$ times that at 180° and that an error of 10° in the scattering angle due to the convergence of the incident beam, which is unavoidable, broadens the displaced components by about 10%. The result of it is that even in the most favourable cases, the Brillouin components cannot be well separated from the central component. In fact, Birus (1938) who adopted the transverse direction in conjunction with an echelon grating for the determination of the relative intensities of the three components, obtained patterns in which the displaced components could be scarcely identified. It is difficult to obtain from his published photographs any reliable information about the actual breadth or the intensity of the components. Both as regards the intensity of scattering and the frequency shift, the backward direction is the most favourable for observation. It is then possible to restrict the convergence of the incident beam to about 5°; but even if the error be as much as 10°, the broadening of the shifted lines is quite negligible and it therefore becomes possible to estimate the actual breadth of the components accurately. Further, as the method enables a great depth of liquid to be utilised, the patterns are more intense and can be recorded in a shorter time than is required for the transverse direction. The chief disadvantage in making observations at 180° to the incident direction is the difficulty for avoiding completely the reflections from the rear end of the experimental tube, which give a spurious central component. But by carefully choosing the glass tube and painting the whole of it except the observation end with enamel black, it is found possible to secure a suitable background, which is nearly as satisfactory as that obtainable with transverse scattering. The experimental tube is made of pyrex glass tubing, 1½″ in diameter and 12″ long, and free from streaks. To one end is fused a thin pyrex glass plate, the other end being drawn out in the form of a horn. The liquid is introduced into the tube and rendered dust-free by distilling it in vacuum by the usual method, the process being repeated until no dust particles could be detected with the tube placed in the track of a narrow beam of sunlight. The rest of the experimental arrangement is the same as that described in the previous paper except that the tube containing the liquid replaces the gas container. During the exposure, the liquid is maintained at room temperature by surrounding it with a water jacket kept in contact with the Wood's tube by metal foils. For experiments at higher temperatures, the water jacket is replaced by a cylindrical electric heater wound on a wide glass tube. The time of exposure for recording the zinc radiations varied from two to four days.

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* Lyshede and Rasmussen (1937) have observed weak satellites for the zinc lines, two satellites at ·108 and ·146 cm.$^{-1}$ for 4680, four at ·127, ·086, ·063 and ·128 cm.$^{-1}$ for 4722 and four at — ·096, — ·056 and ·100 and ·163 cm.$^{-1}$ for 4810. These satellites are so weak that 1 to 4 hours are required to record them with observable intensity, whereas the principal line is registered strongly in a minute. In view of the extreme feebleness of the satellites and the small shift from the principal line, they do not appear in the scattered light.

D: Polarisation Measurements.—Gross (1930), Rao (1935), Birus (1938) and Mitra (1940) have measured the state of polarisation of the components by interposing a Nicol in the path of the transversely scattered light and recording two spectra, one with the vibration axis of the Nicol vertical and the other with the axis horizontal. This arrangement is, however, unsatisfactory as it is difficult to maintain the source at constant running condition for both the exposures, especially as the time of exposure required is very great. It is of advantage to record both the horizontal and the vertical components simultaneously. For this purpose, the experimental arrangement given in Fig. 1 is made use of. The light from a high-vacuum horizontal mercury arc A with water-cooled cathode is let fall on a Wood's tube T as a parallel beam by using a series of parallel vanes of blackened metal plates arranged in layers. The breadth of the metal plate is 50 mm. and the distance between successive plates 4 mm., giving a convergence angle of 4½°. The corresponding convergence error is less than ·1%. Light scattered in the transverse direction by the liquid is focussed by means of a condenser L on the widely opened slit of a Hilger constant-deviation spectroscope. A glass Lummer plate P is placed between the collimating lens and the prism and a double-image prism D.P., of 1″ aperture, is interposed between the camera lens and the photographic plate in such a way that the horizontal and the vertical components are recorded side by side. As the dispersions of the Lummer plate and of the constant-deviation prism are mutually perpendicular, the polarisations produced at the optical surfaces partially annul each other, the resultant effect as determined experimentally using unpolarised light being the enhancement of the intensity of the vertical component by 12%. As a test of the arrangement, the horizontal and the vertical components of the interference pattern for light diffused transversely by a critical mixture of methyl alcohol—normal hexane were recorded. The pattern obtained is reproduced as Fig. 10 *a* in Pl. XI. It will be noticed that the horizontal component is extremely weak in comparison with the vertical; a microphotometric estimate of the intensity of the central components in the

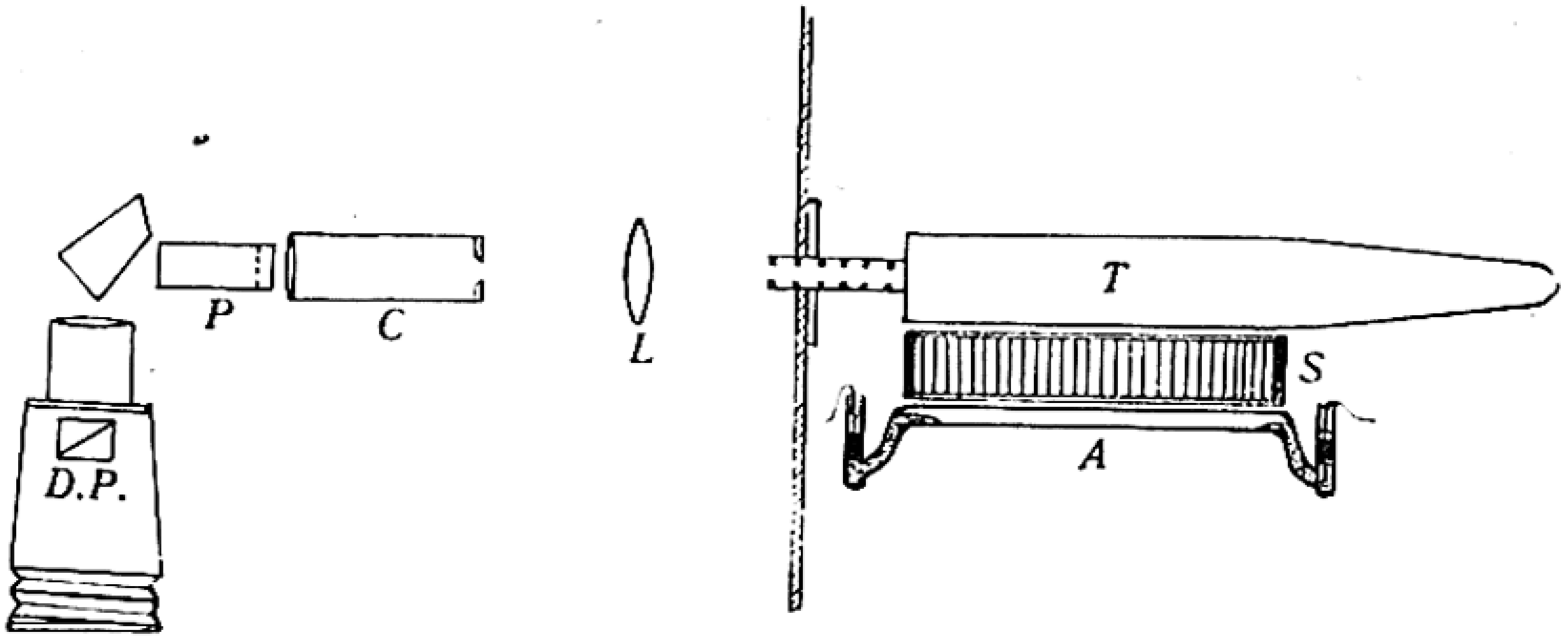

FIG. 1. Experimental Arrangement for Polarisation Studies

two pictures gives the depolarisation ratio as ·02, which is in good agreement with the value obtained non-spectroscopically (Krishnan, 1935). The state of polarisation of the spectral components in the light scattered by cyclohexane, benzene, tetralin, phenol and glycerine has been studied.

3. *General Statement of Results*

The present paper describes the results obtained with four liquids having low depolarisation and low viscosity, *viz.*, carbon tetrachloride, cyclohexane, ethyl ether and ethyl alcohol; three others with moderate depolarisation and viscosity, *viz.*, acetone, iso-butyric acid and water, and also three liquids with a high depolarisation, *viz.*, benzene, phenol and tetralin. The interference patterns have been recorded with all radiations of the zinc-mercury arc scattered by these liquids. The records for the 4810 A.U. line of zinc obtained with a 5 mm. separation for the etalon are reproduced in Figs. 7 and 8 in Pl. X. The main features of the patterns are the following:

(1) At room temperature, the Brillouin components are fairly sharp and well defined in all liquids except in the case of carbon tetrachloride and ethyl ether in which they are broader.

(2) In well-exposed spectra of carbon tetrachloride, ether, alcohol, acetone and iso-butyric acid, a feeble component having twice the usual Brillouin displacement is observed. Its intensity is not more than 1/50th of the first order component as may be seen from the microphotometric records for alcohol (Fig. 4 *a*). Patterns of these liquids taken with 3 mm. separation for the interferometer plates showed no indication of any component with thrice the usual Brillouin displacement. In the case of aromatic liquids, the general background due to orientation scattering prevents the observation of any spectral components other than those of the first order.

(3) The general background superposed on the pattern increases in intensity with increasing depolarisation of total scattering. It however, shows a marked decrease with increasing viscosity of the liquid. For instance, with tetralin which has a high viscosity, the background is less intense than for benzene, even though the depolarisation of the light scattered by the former liquid is greater than that by benzene.

(4) In all liquids there is an undisplaced central component, the intensity of which relative to the Brillouin components varies from liquid to liquid.

(5) There is a continuum connecting the central and the Brillouin components of which the intensity is greater, the nearer the temperature of the liquid is to its boiling point. It may be clearly seen in the interference

patterns for ethyl alcohol, ethyl ether and isobutyric acid in which the central component is weak (see Figs. 7 *e*, *f*, *i*, *k* and *l*). This continuum is to be distinguished from the general background covering the whole pattern due to orientation scattering; in fact, in aromatic liquids in which the rotation wing is very intense, the continuum between the components is masked by the latter.

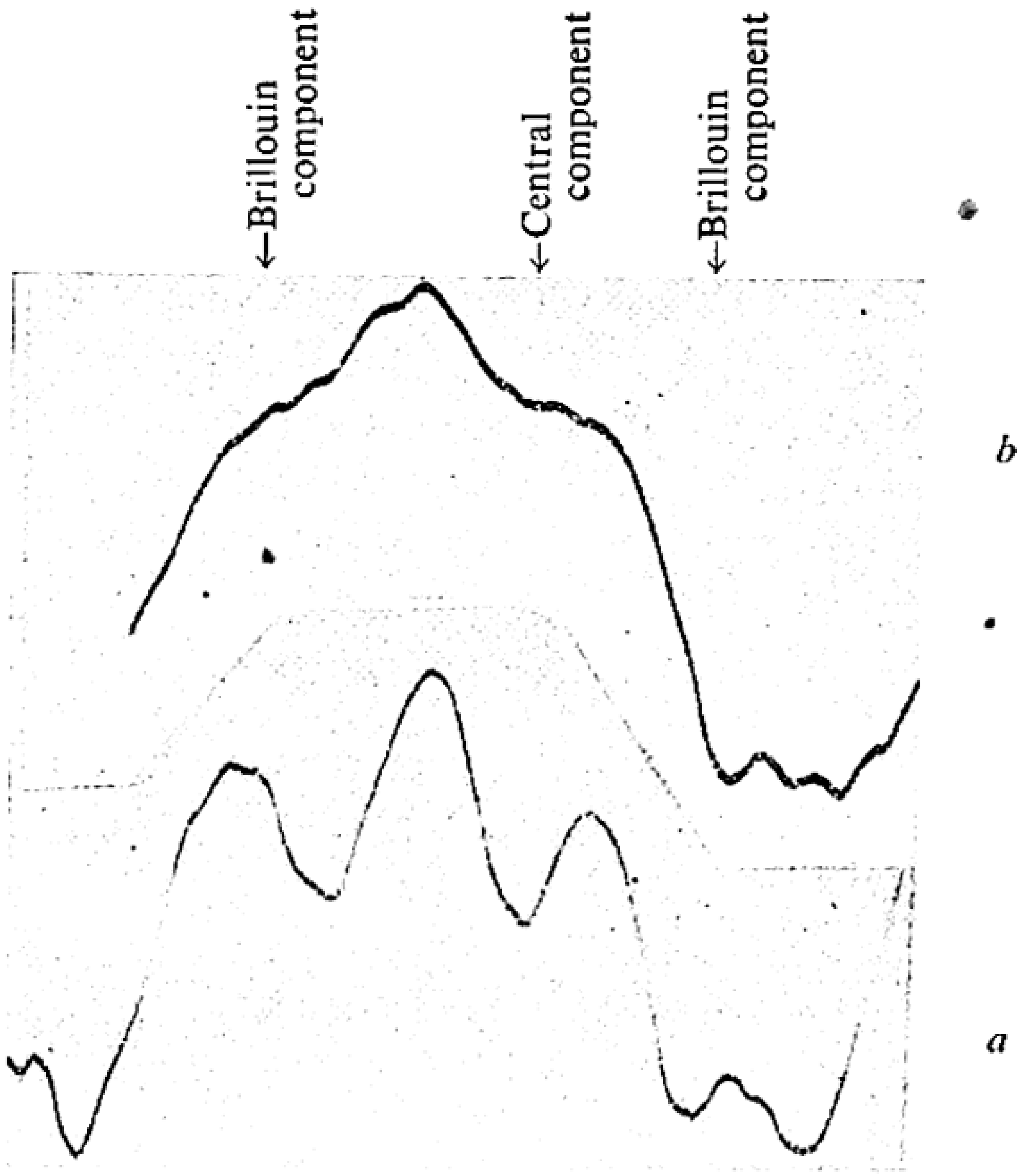

FIG. 2. Microphotometric Curves for Acetone Scattering (*a*) at 28° C. and (*b*) at 54° C.

4. *The Effect of Temperature*

In order to study the effect of temperature on the breadth and the intensity of the three components, four typical liquids namely, acetone, ethyl alcohol, isobutyric acid and phenol have been chosen. The patterns of the scattered light were recorded for the high and low temperatures under exactly identical conditions. The effect of an increase of temperature in the four cases may be summarised as follows:—

(1) The Brillouin components in acetone become broader and shift towards the centre. As the separation between the components is small at the higher temperature, they appear as if they merge into one another (see Fig. 2). This effect is similar to the one observed by Raman and Rao (1935) in carbon tetrachloride.

(2) In the case of ethyl alcohol and iso-butyric acid (see Fig. 7 *e* and *f*, *k* and *l*), the rise of temperature is followed by a decrease in the intensity of the central component and an increase in that of the continuum. Both these liquids were examined near the boiling point; this involved raising the temperature of the acid by more than 120°. At the boiling point, the central component is scarcely present. The Brillouin components which are very intense even at the room temperature do not show any perceptible increase of intensity, though a slight broadening and a smaller frequency shift are noticeable. It appears reasonable to conclude that the increased density scattering which should result from the increased compressibility of the liquid at the higher temperature appears as an intensified continuum between the components.

(3) The intensity of the shifted components for supercooled phenol at 25° C. is very low. As the temperature is raised to 162° C., they gain considerably in intensity and remain sharp and well-defined except, at the very highest temperature, as illustrated in Fig. 8 in Pl. XI. At the same time, the central component becomes weaker. At the higher temperatures, a continuum also makes its appearance.

These results indicate that with increase in the mobility of the molecules following an increase of temperature, a part of the intensity of the central component gets released in all cases. The scattering power of the liquid also increases due to an increase in the compressibility of the medium. When the viscosity of the liquid is great as in phenol, the intensity thus made available is divided between the two coherent modified components. If the liquid is highly mobile, there is no enhancement of the intensity of the Brillouin components; but the released intensity gets distributed in the continuum. The diminution in the frequency shift of the Brillouin components with rise of temperature may be explained as due to the increase in the adiabatic compressibility and consequent diminution of the sound velocity in the medium.

5. *Polarisation Studies*

The polarisation pictures obtained for cyclohexane, benzene, tetralin, glycerine and phenol at 45°C. and with 4358 A.U. radiations of the mercury arc are reproduced in Figs. 10 *a*–10 *f* in Pl. XI. Similar pictures were recorded for the 4046 A.U. as well. In all the patterns the fringes are seen in the horizontal component but their intensity is always less than in the vertical component. They are extremely weak in cyclohexane as we should expect from the low depolarisation in the liquid. In benzene, phenol and tetralin, the fringes in both the components are superposed on an intense background due to rotational scattering. In none of these pictures are the Brillouin components clearly separated from the central line; the fact that these are polarised may only be inferred from the relative intensities of the edge of the fringes in the horizontal and vertical patterns. The present investigation however, clearly establishes that the central component in the spectral pattern of the scattered light is partially polarised, the extent of depolarisation being very small either when the liquid is very mobile (*e.g.*, benzene) or when the depolarisation of the total scattering is low (*e.g.*, cyclohexane). This result modifies the conclusions of Rao (1935) and Birus (1938) based on observations with carbon tetrachloride, toluene and carbon disulphide, namely, that all the three spectral components are completely polarised. That the above authors have failed to notice the fringes in the horizontal component is probably because the pictures obtained by them are not sufficiently intense to record them; the fringes are very weak owing to the low viscosity in the case of toluene and carbon disulphide and owing to the low depolarisation in the case of carbon tetrachloride.

For making a correct estimate of the partial polarisation of the undisplaced central component, it is evidently necessary to deduct from the maximum intensity in the fringes that of the background, namely the intensity at the point of minimum illumination in the same, this being done separately for the vertical and the horizontal components. The ratio of the maxima of illumination in the horizontal and vertical components thus duly corrected, is indicated by ρ_{centre} and shown in column 6 of Table I, while $\rho_{background}$ which is the ratio of the minima of illumination in the two components is shown in column 7. The intensity ratio of the minimum to the maximum of illumination in the horizontal component is also given in column 8; complete invisibility of the fringes in this component would correspond to a value unity for this ratio. To enable the significance of these results to be appreciated, the depolarisation of the transversely scattered light as determined

TABLE I

Liquid	Prismatic Spectroscope			Lummer Plate			
	Temperature	$\rho_{wide\ slit}$	$\rho_{narrow\ slit}$	Temperature	ρ_{centre}	$\rho_{back\text{-}ground}$	Intensity ratio of background to centre
Benzene . .	30°	·44	·12	45°	·10	·70	·90
Tetralin . .	30°	·54	·45	45°	·38	·78	·84
Phenol . .	45°	·66	·46	45°	·42	·75	·79
Glycerine . .	20°	·33	·30	45°	·25	. .	. .

by an ordinary prismatic spectroscope, using a wide and a narrow slit respectively, are shown in columns 3 and 4 of the table. The former expresses the depolarisation of the total scattering by the liquid, and the latter the depolarisation after the rotational Raman scattering is excluded as completely as is possible with the instrument employed. These values are taken from papers by Saxena (1938) and Sunanda Bai (1941).

The data shown in Table I are very significant. It is seen that the depolarisation of the central fringe in the Lummer pattern is of the same order of magnitude as the depolarisation of the total scattering by the liquid *after excluding the rotational Raman scattering by its molecules.* The values of ρ_{centre} are on the other hand, smaller than $\rho_{wide\ slit}$. It will be noticed that the latter is greater for benzene than for glycerine, while the situation is reversed in respect of both ρ_{centre} and $\rho_{narrow\ slit}$. It is thus clear that the partial polarisation of the central component in the Lummer pattern has the same physical origin as the partial polarisation of the light diffused by the liquid when the rotational Raman scattering is excluded, in other words that it arises from the presence in the scattered light of a completely depolarised Q-branch of the rotational scattering. The fraction of the latter appearing as a Q-branch instead of in the rotation " wings " may be expected to become larger with increasing viscosity of the liquid, as a greater proportion of the molecules would then occupy practically fixed orientations. It follows that with increasing viscosity of the liquid, the intensity ratio of the background to the centre in the pattern should decrease. This is in agreement with observations as shown both by the photographs and by the measurements of intensity recorded in column 8 of Table I.

It is evident from the photographs that the Brillouin components for all the liquids exhibit a high degree of polarisation. The experimental evidence is however, not decisive on the question whether their polarisation is *total* as suggested by theory. Indeed, there is some evidence suggesting that in the case of mobile liquids with anisotropic molecules they may be only partially polarised. This is shown, for instance, by the fact that the central bright fringe in the horizontal component of the Lummer pattern in aromatic liquids is not very sharp. Further, if the Brillouin components had been fully polarised, we should have found that ρ_{centre} is somewhat greater than $\rho_{narrow\ slit}$ in every case; for these components are included in the latter and excluded from the former. Actually, the measurements show that ρ_{centre} and $\rho_{narrow\ slit}$ are about equal for all the liquids. Another anomaly which is noticed is that $\rho_{background}$ in every case is somewhat smaller than the value 6/7 indicated by theory for pure orientation scattering. Whether these anomalies are real or whether they arise from the unavoidable difficulties of experimentation must remain for the present an open question. These remarks however, do not affect the validity of the main conclusions already stated.

6. *The Relative Intensity of the Brillouin and the Undisplaced Components*

In order to test the experimental arrangements, the light scattered by water, ethyl alcohol and benzene were examined both in the transverse and the longitudinal directions. Figs. 3 *a-c* are the microphotometric records of the 4358 A.U. of the mercury arc after scattering by water in these two directions and that of 4810 A.U. of the zinc arc for the backward direction only. The transverse scattering could not be examined by the zinc lines, as it is very weak. The corresponding spectra are reproduced in Fig. 9, Pl. XI. It will be seen that the central component is clearly present in all the three patterns, though definitely weaker than the displaced components. For reasons already mentioned, with the mercury radiations, the background for the transverse direction is very intense; it is distinctly less with the longitudinal scattering and almost completely absent when the zinc arc is employed. Due to the presence of this background of varying intensity, it is not possible

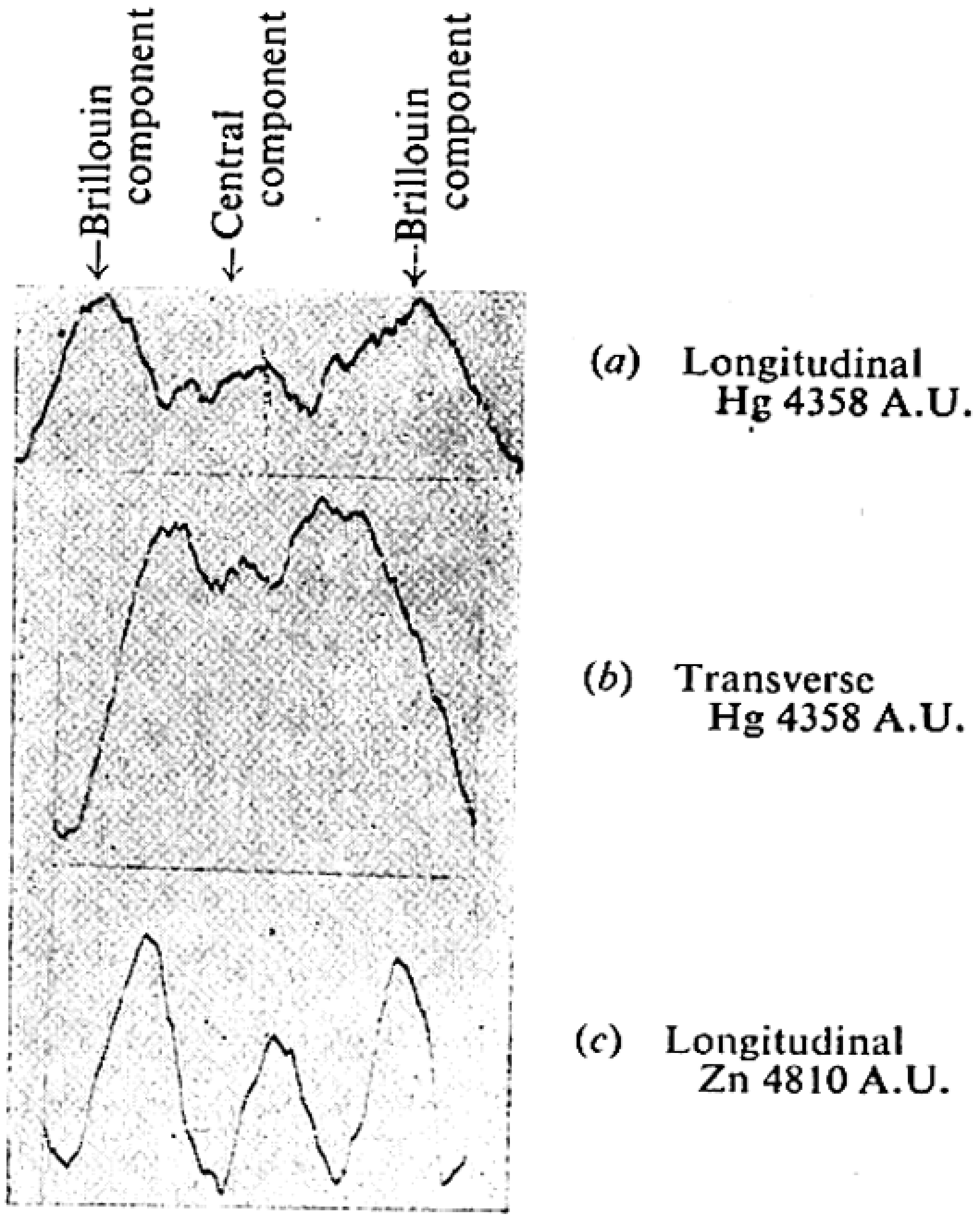

FIG. 3. Microphotometer Curves for Water Scattering

to make an accurate estimate of the ratios of intensities of the central components to the displaced components and compare them in the three cases. For benzene and ethyl alcohol the frequency shifts of the Brillouin components are relatively small and hence in the transverse scattering, the three components are scarcely separated from each other. However, an examination of these pictures due to the mercury and the zinc radiations gives the impression that the central line is present in them with almost the same relative intensity as in the backward scattering. In view of these results it is assumed that parasitic reflections do not sensibly affect the relative intensity of the components even in weakly scattering liquids.

Figs. 4 *a* to *g* give the microphotometric tracings of the 4810 A.U. of the zinc arc after it is scattered backwards by carbon tetrachloride, cyclohexane,

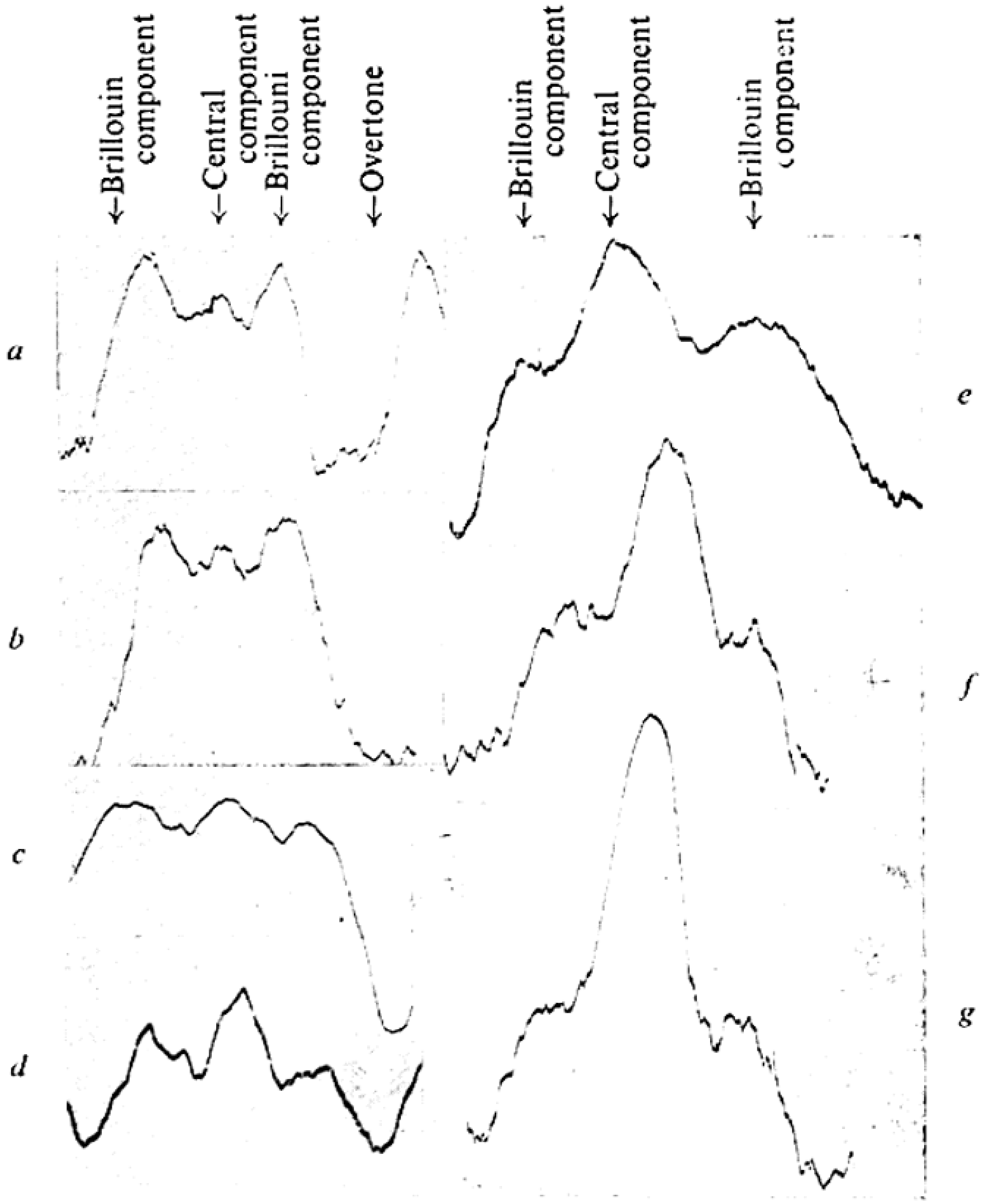

FIG. 4. Microphotometric Curves for Liquids

(*a*) Ethyl alcohol.
(*b*) *iso*-Butyric acid.
(*c*) Ethyl ether.
(*d*) Cyclohexane.
(*e*) Carbon tetrachloride.
(*f*) Tetralin.
(*g*) Benzene.

ethyl ether, ethyl alcohol, *iso*-butyric acid, benzene and tetralin. The ratio of the intensity of the central component I_C to the total intensity of the two Brillouin components, I_B, is estimated from these records by making use of the appropriate density-log intensity curve and listed in the last column of Table II. The adiabatic and isothermal compressibilities β_ϕ and β_t, η, the

TABLE II

Temperature of Observation $\backsimeq$ 25° *C.*

Liquid	η in poises	$\beta_t \times 10^6$	$\beta_\phi \times 10^6$	ρ_∞	ρ_0	$\frac{I_0}{I_D}$	$\frac{I_Q}{I_D}$	$\frac{I_C}{I_B}$
Carbon tetrachloride	·0084	115	78	·052	·013	·12	·03	·84
Ethyl alcohol ..	·0099	115·8	97·2	·054	·015	·13	·04	·39
Ethyl ether ..	·0021	196·7	146·9	·081	·026	·20	·06	·45
Cyclohexane ..	·0082	125	85	·080	..	·20	..	·65
Water ..	·0089	46·0	45·6	·088	..	·21	..	·36
Acetone ..	·0029	127	91	·20	·06	·56	·135	·79
Iso-butyric acid ..	·0133	..	91·5	·35	·15	1·28	·4	·45
Benzene ..	·0059	98·7	68·6	·44	·12	1·92	·29	·97
Tetralin ..	·0200	..	48·1	·54	·45	3·16	1·95	1·20

viscosity of the liquid at 25° C. and the wide and narrow slit values of depolarisation ρ_∞ and ρ_0 are given in columns 2 to 6. I_0/I_D the ratio of the orientation scattering to the density scattering and I_Q/I_D, where I_Q is the fraction of the former falling on the Q-branch calculated from the ρ_∞ and ρ_0 values, are given in columns 7 and 8. It should be mentioned that the ratio I_C/I_B is determined from the peak intensities of the three components and does not take into account their relative breadths. As the displaced components in some of these liquids are broader than the central one, these values give only the upper limit to the intensity ratio. Moreover, the presence of the continuum between the components makes the determination of the intensities less accurate. Due to these causes and the possibility of traces of parasitic light still being present, the experimental values may be slightly higher than the true ones.

7. *Discussion of the Results*

It will be seen from Table II that several of the liquids listed in it, *viz.*, carbon tetrachloride, cyclohexane, acetone, benzene and tetralin, give a central component which is brighter than either of the Brillouin components. As the scattering power is large for these liquids, the probability of parasitic light vitiating the results is much less than in the case of ether, alcohol and water for which weaker central components are registered. The intensity of the central component may evidently be due in part to the Q-branch of the orientation scattering coinciding with it. A comparison of the values shown in the seventh and ninth columns of the table shows that while for liquids of low depolarisation, *viz.*, carbon tetrachloride, ether, alcohol and tetralin, I_C/I_B is much greater than I_Q/I_D, the position is reversed in the case of *iso*-butyric acid, benzene and tetralin. An estimate of the intensity of the Q-branch, which may be regarded as an upper limit, may be made from the known values for ρ_∞ and ρ_0. The ratio $\frac{I_Q}{I_D}$ thus calculated is shown in column 8. It is seen that in every case except the two most viscous liquids *iso*-butyric acid and tetralin which have also the largest depolarisation, $\frac{I_Q}{I_D}$ is always much less than $\frac{I_C}{I_B}$. We are thus obliged to conclude that in the case of most ordinary liquids, the appearance of a central component cannot be explained as being principally due to the presence of a Q-branch for the orientation scattering. For the greater part, therefore, it must arise in some other way.

Landau and Placzek (1934) have tentatively suggested that the ratio of the central component to the total intensity of the Brillouin components arising from density fluctuations alone is given by $\gamma - 1$, where γ is the ratio of the isothermal to the adiabatic compressibility or the ratio of the specific heats of the liquid. This suggestion appears to be based on the assumption that the total density scattering of light in a liquid takes place in two steps; the first part arising as a result of the fluctuations taking place adiabatically, which appears as two equally intense displaced components and the second part due to a further increase in the density fluctuations during the restoration of thermal equilibrium in the medium, which falls on the central component. The total scattering will thus be represented as an isothermal process. Birus (1938) claims to have verified the relation of Landau and Placzek in the cases of ethyl alcohol, water and toluene. He finds support to his results from his observation that the central component is completely polarised. We have already seen that the latter statement is incorrect, and that the experimental method adopted by him cannot give the true estimate of the relative intensitities of the central and the Brillouin components.

The fundamental assumption on which the theory of Landau and Placzek is based, namely that the total intensity of the scattering in a liquid is given by the isothermal formula has been shown by Sunanda Bai in a paper appearing in these *Proceedings* to be not in accord with the actual facts. She has observed that the intensity of light scattered transversely in many liquids is intermediate between those calculated on the assumption that the density fluctuations take place in an adiabatic and an isothermal fashion.

That the considerations on which the Landau-Placzek theory is based are invalid is also indicated by the figures in Table III giving respectively the observed ratio of intensities and that calculated from the specific heats.

TABLE III

Ratio of Intensity of the Central Components to those of the Brillouin Components

Liquid	As calculated* from the Placzek-Landau Formula	As Observed	Liquid	As calculated from the Placzek-Landau Formula	As Observed
Carbon tetrachloride	·48	·84	Cyclohexane	·47	·65
			Water	·01	·36
Ethyl alcohol	·18	·39	Acetone	·39	·79
Ethyl ether	·34	·45	Benzene	·32	·97

* γ is calculated from the adiabatic and isothermal compressibilities given by Philips (1939) and Tyrer (1914).

Summary

A detailed interferometric study has been made of the spectral character of the monochromatic light in several dust-free liquids. The structureless radiations of the zinc arc, namely 4680, 4722 and 4810 A.U. are employed, and the light scattered backwards is analysed by a Fabry-Perot etalon. The liquids used are carbon tetrachloride, cyclohexane, ethyl ether, ethyl alcohol, water, *iso*-butyric acid, acetone, benzene, tetralin and phenol. Besides the two Brillouin components and an undisplaced central component, a continuum extending between these components is also noticed. This continuum is particularly intense in low boiling point liquids, like ethyl ether and ethyl alcohol. The displaced components are sharp and well defined for most of the liquids at the room temperature; but they become broad when the temperature is raised to the boiling point. The first overtone of the displaced component is also observed to be weakly present in ether, ethyl alcohol, acetone and carbon tetrachloride. The effect of increase of temperature is to lower the intensity of the central component. When the viscosity of the liquid is high, as in the case of phenol, the intensity thus set free enhances the intensity of the displaced components. When the liquid is very mobile, there is no appreciable increase in the intensity of the Brillouin components; but the continuum between these components gains intensity considerably. In the light scattered transversely by cyclohexane, benzene, tetralin, phenol and

FIG. 5 Hg ARC. FIG. 6 Zn ARC.

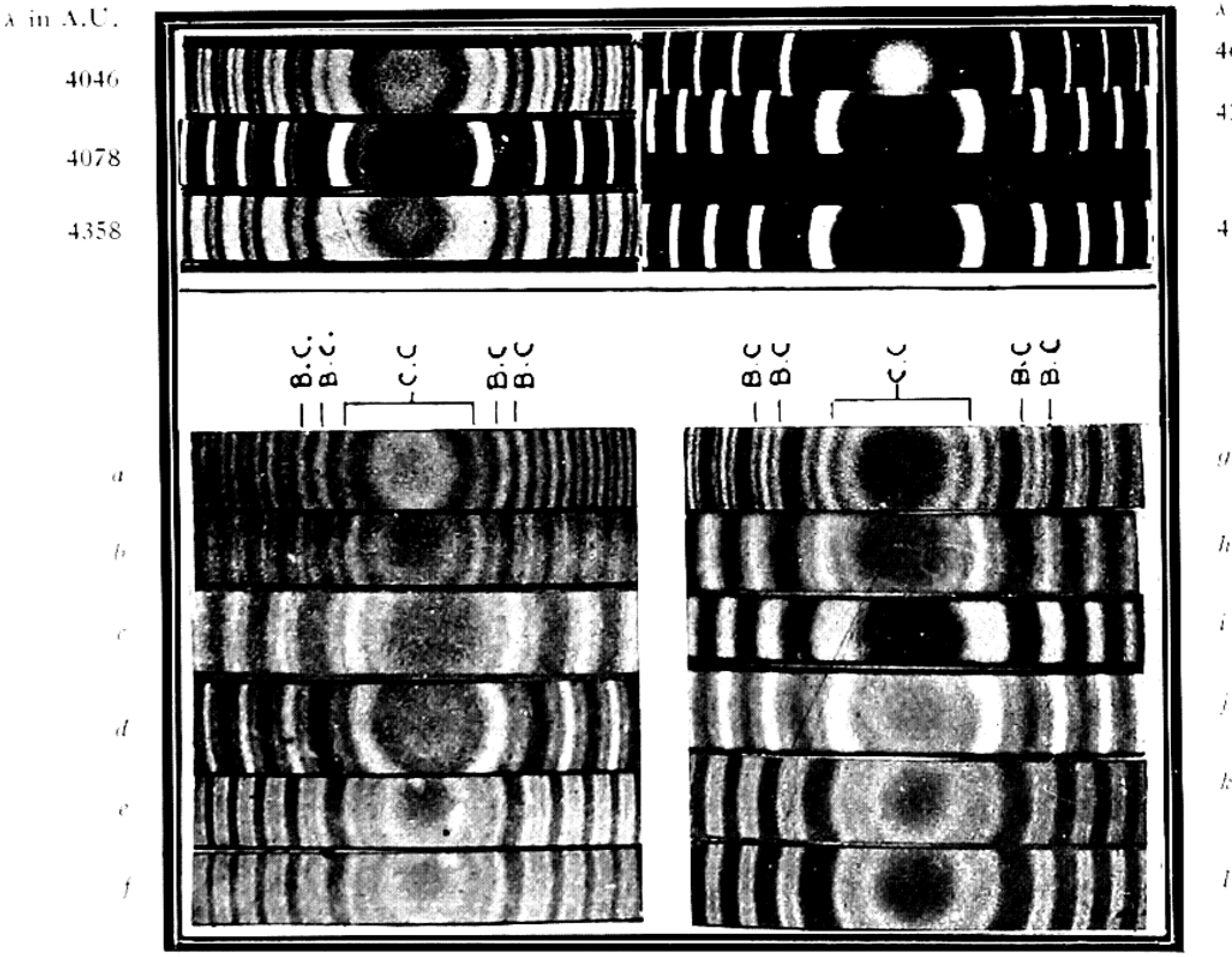

FIG. 7. Interferometer Patterns of Liquid Scattering

a. Water (30°)
b. Cyclohexane (30°)
c. Carbon tetrachloride (25°)
d. Benzene (28°)
e. Ethyl alcohol (25°)
f. Ethyl alcohol (65°)
g. Acetone (28°)
h. Acetone (54°)
i. Ethyl ether (30
j. Tetralin (30°)
k. *iso*-Butyric acid
l. *iso*-Butyric acid

FIG. 8
Phenol

FIG. 9. Water

a. Hg. 4358

b. Transverse Scattering

c Longitudinal Scattering

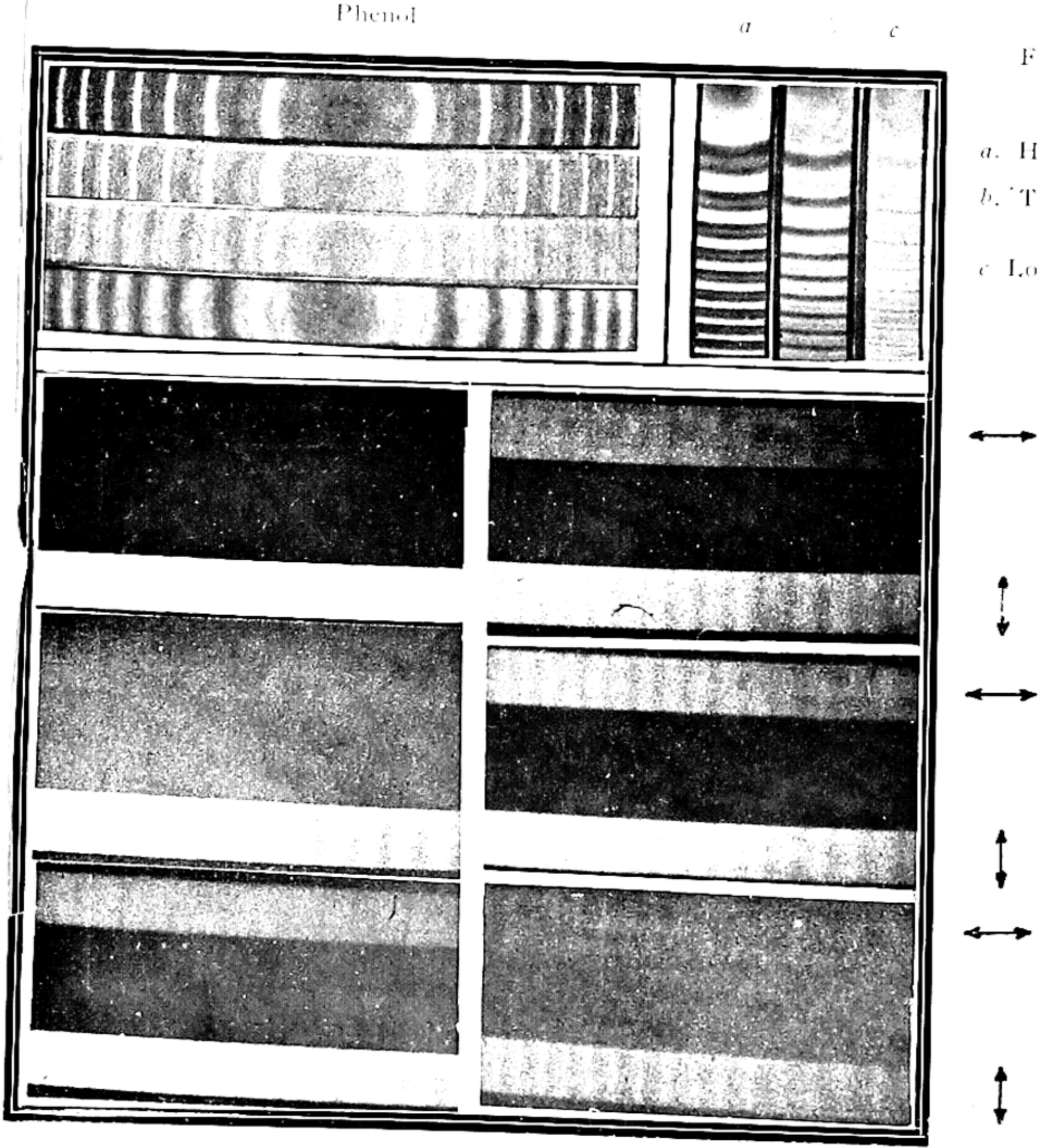

FIG. 10. Polarisation Pictures

a. Methyl alcohol-*n*.Hexane mixture. *b*. Cyclohexane. *c*. Benzene (45°). *d*. Phenol (45°). *e*. Tetralin (45°). *f*. Glycerine (45°).

glycerine, the central component is partially polarised, the ratio of depolarisation being however, smaller than that of the total scattering. The difference between these two ratios depends on the viscosity, being less the higher the viscosity of the liquid. The ratio of the intensity of the central component to that of the Brillouin components is determined for these liquids and is found to differ widely from the values to be expected from the Landau-Placzek hypothesis regarding the origin of the central line. It is remarked that the interferometric study of light scattering in effect enables us to find the frequency spectrum of the fluctuations of optical density in the fluid.

In conclusion the author takes this opportunity to thank Prof. Sir C. V. Raman, for suggesting the problem and for his keen and inspiring interest in the course of these investigations.

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THE SCATTERING OF LIGHT IN LIQUIDS

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Part I. Theoretical

1. *Introduction*

In spite of numerous papers that have appeared on scattering of light by liquids, the position of the subject, both from the point of view of theory and experiment is far from being satisfactory. The chief difficulty in formulating a comprehensive theory for the scattering of light by liquids is, that the structure of liquids with which the latter is intimately connected, is still not well understood. The theory of light scattering which holds the field at present is the one based on the probability of fluctuations in a continuous medium put forward by Einstein and Smoluchouski, the application of which leads to the following expression for the intensity of light scattered in the transverse direction:

$$I = \frac{\pi^2}{2}\,\frac{RT\beta}{N\lambda^4}\,(\mu^2 - 1)^2\,\frac{(\mu^2 + 2)^2}{9}\,\frac{6\,(1 + \rho)}{6 - 7\,\rho}, \tag{1}$$

where R, T, β, N and ρ are respectively, the gas constant, absolute temp., isothermal compressibility, Avagadro-number, and depolarisation ratio. The fundamental assumptions involved in the derivation of the above expression are that the medium is made up of a large number of volume elements, each of which is small compared to the wavelength of light, but sufficiently large so as to contain an appreciable number of molecules (of the order of fifty) and that the changes in number taking place in the neighbouring volume elements are uncorrelated. The fluctuation in number in each volume element which causes density scattering is given by the Einstein-Smoluchouski expression $\overline{\Delta\nu^2} = \frac{RT\beta}{NV}\,\nu^2$ where $\overline{\Delta\nu^2}$ is the mean square of the deviation of the number of molecules per unit volume from its mean value ν and β is the isothermal compressibility. It is further assumed that the density ρ and the refractive index μ of the medium are connected together by the Lorentz-Lorenz relation $\frac{\mu^2 - 1}{\mu^2 + 2} = C\rho$, where C is a constant.

As in the case of gases the whole process is treated as isothermal. The factor $\frac{6\,(1+\rho)}{6-7\,\rho}$ is the contribution due to the anisotropy of the molecule and the only assumption involved in obtaining this factor is that the orientation scattering is depolarised to an extent of 6/7. The latter assumption has been fully substantiated by experimental observations.

Experimental determination of the absolute intensities of light scattered by a few liquids like water, ether and benzene by Martin (1920), Martin and Lehrmann (1922), Cabannes and Daure (1927), and Peyrot (1936), and the relative intensities of a large number of liquids by Krishnan (1925), Banerjee (1927) and Peyrot (1926), have shown that the observed intensities are always lower than those calculated from equation (1). Ramanathan (1927) has explained this discrepancy by assuming that the factor μ^2+2 in the Lorentz relation arising from the influence of external volume elements on any particular volume element considered, is constant. Thus by using the relation $\mu^2-1=C\,\rho$ he has derived an expression for the intensity of transversely scattered light, which differs from the former in not having the factor $\frac{(\mu^2+2)^2}{9}$. This shows a slightly better agreement with observed facts, but in some cases it gives values which are higher than the latter.

Quite apart from these difficulties, serious objections to the above theories arise when one considers the results of recent investigations of the fine structure of unmodified light scattering by liquids. It is now a well-established fact that a significant part of the density scattering in liquids consists of two well-defined Brillouin components, the frequency shift of which from the main line corresponds to a velocity for the thermal waves equal to the acoustic velocity in the medium. This sugggests that fluctuations taking place in the neighbouring volume elements are at least partly coherent as in a crystal and the density scattering arising from such coherence should be treated strictly as adiabatic.

There is reason to believe that another part of the density scattering falls on the undisplaced central line and the remainder appears as a continuum between the three components. As has been pointed out by Venkateswaran (1942) in a earlier paper, the latter two parts depend on the extent of disorder in liquids and is akin to scattering in gases, and may be treated isothermally; secondly, recent investigations by Raman and Venkataraman (1939) on the piezo-optic coefficients of liquids have shown that the Lorentz-Lorenz refraction formula on which the derivation of the intensity expression for light scattering is based, completely breaks down for all liquids examined by them. They have found that the variation of the refractive index indicated by the above expression to be invariably larger than the observed values for changes of pressure as well as of temperature, these deviations being most pronounced for liquids having high refractive index and high optical anisotropy.

In the present communication a method of deriving the intensity of light scattered by liquids taking into account the preliminary considerations set forth above is indicated and the results are compared with fresh experimental data obtained for eleven representative liquids.

2. *Thermodynamical derivation of the formula for the intensity of transversely scattered light*

Let us consider the liquid medium to be continuous, and subdivide it into a large number of volume elements. To find out the fluctuations in the thermodynamical properties of this continuous medium, we have to find out the probability for one of the volume elements to be out of equilibrium with the remainder. If W represents the work that has to be done in transforming this volume element from the equilibrium state, to any other state, through a reversible process, the probability that the volume element may spontaneously reside in the latter state is proportional to $e^{\frac{-W}{kT}}$

This fact is given by the relation $\omega \propto e^{\frac{-W}{kT}}$ (1)

where k and T are respectively the Boltzmann constant and absolute temperature. If the energy of the volume element increases by ΔE, and its entropy and volume by $-\Delta$S and ΔV, as a result of transformation we have

$$W = \Delta E - T\Delta S + p\,\Delta V \tag{2}$$

where T and p are the mean temperature and pressure of the volume element.

If the energy E is regarded as a function of entropy S and volume V, we may write ΔE as follows:

$$\Delta E = \frac{\partial E}{\partial S}\Delta S + \frac{\partial E}{\partial V}\Delta V + \frac{1}{2}\left[\frac{\partial^2 E}{\partial S^2}(\Delta S)^2 + 2\frac{\partial^2 E}{\partial S \partial V}\Delta S\,\Delta V + \frac{\partial^2 E}{\partial V^2}(\Delta V)^2\right] \tag{3}$$

Using the relation $T = \left(\frac{\partial E}{\partial S}\right)_V$ and $p = -\left(\frac{\partial E}{\partial S}\right)_V$ and combining (3) with (2) equation (1) becomes

$$\omega \propto e^{\frac{\Delta p\,\Delta V - \Delta S\,\Delta T}{2\,kT}} \tag{4}$$

The four variables involved in the above expression are p, V, S and T, and if we choose any two of these as independent variables, we can find out the fluctuations in the other two.

For isothermal process we have to take V and T as independent variables. Then we have

$$\left.\begin{aligned} \Delta S &= \left(\frac{\partial S}{\partial T}\right)_V \Delta T + \left(\frac{\partial S}{\partial V}\right)_T \Delta V \\ &= \frac{C_v}{T}\,\Delta T + \left(\frac{\partial p}{\partial T}\right)_V \Delta V \\ \text{and } \Delta p &= \left(\frac{\partial p}{\partial T}\right)_V \Delta T + \left(\frac{\partial p}{\partial V}\right)_T \Delta V \end{aligned}\right\} \tag{5}$$

Substituting (5) in (4) we have

$$\omega \propto e^{\frac{(\Delta V)^2}{2kT}\left(\frac{\partial p}{\partial V}\right)_T} \cdot e^{-\frac{C_v}{2kT^2}(\Delta T)^2} \tag{6}$$

Since V and T are chosen as independent variables, the fluctuations of V and T take place independently, and we have $\overline{\Delta V\,\Delta T} = 0$. By comparing (6) with the Gaussian error function we get the following relation

$$(\overline{\Delta V})^2 = -kT\left(\frac{\partial V}{\partial p}\right)_T = \frac{RT\,\beta_T}{NV} \tag{7}$$

$$(\overline{\Delta T})^2 = \frac{kT^2}{C_v}. \tag{8}$$

On the other hand for the adiabatic process we have to take V and S as independent variables, and we have

$$\left.\begin{aligned} \Delta p &= \left(\frac{\partial p}{\partial V}\right)_S \Delta V + \left(\frac{\partial p}{\partial S}\right)_V \Delta S \\ \Delta T &= \left(\frac{\partial T}{\partial V}\right)_S \Delta V + \left(\frac{\partial T}{\partial S}\right)_V \Delta S \\ &= \frac{T}{C_v}\,\Delta S - \left(\frac{\partial p}{\partial S}\right)_V \Delta V \end{aligned}\right\} \tag{9}$$

Again substituting (9) in (4) we get

$$\omega \propto e^{\left[\left(\frac{\partial p}{\partial V}\right)_S \Delta V^2 - \frac{T}{C_v}(\Delta S)^2 + 2\left(\frac{\partial p}{\partial S}\right)_V \Delta S\,\Delta V\right]\Big/2kT} \tag{10}$$

and as before, taking $\overline{\Delta S\,\Delta V} = 0$
we obtain

$$(\overline{\Delta V})^2 = -kT\left(\frac{\partial V}{\partial p}\right)_S = \frac{RT\beta_S}{NV} \tag{11}$$

$$(\overline{\Delta S})^2 = C_v k \tag{12}$$

Expressions (7) and (11) are similar excepting that the compressibility in one case is isothermal and in the other adiabatic.

The general expression for the intensity of light scattered by an element of volume V in the transverse direction is given by the expression

$$I = \frac{\pi^2}{2}\frac{V^2}{\lambda^4}(\overline{\Delta\epsilon})^2 \tag{13}$$

where $(\overline{\Delta\epsilon})^2$ is the mean square of the variation of the dielectric constant caused by the fluctuations of density in the medium. Since the variation of the dielectric constant at any particular point is entirely dependent on the variation of density at that point, we have the relation

$$\Delta\epsilon = \frac{d\epsilon}{dV}\Delta V. \tag{14}$$

$$\text{Therefore } (\overline{\Delta\epsilon})^2 = \left(\frac{d\epsilon}{dV}\right)^2 (\overline{\Delta V})^2 \tag{15}$$

Since $V\rho$ (where ρ is the density) is constant for the medium

$$dV = -V\frac{d\rho}{\rho}. \tag{16}$$

Combining (16) with (15) and substituting this value of $(\overline{\Delta\epsilon})^2$ in (13) we obtain

$$I = \frac{\pi^2}{2\lambda^4}\rho^2\left(\frac{d\epsilon}{d\rho}\right)^2(\overline{\Delta V})^2. \tag{17}$$

Again assuming the relation

$$\frac{d\epsilon}{\partial\rho} = \frac{2\mu}{\beta\rho}\frac{\partial\mu}{\partial p} \tag{18}$$

and substituting for $(\overline{\Delta V})^2$ from (7) and (11) respectively, we have the general expressions for the isothermal and adiabatic process namely:

$$I_{iso} = \frac{\pi^2}{2}\frac{RT}{N\lambda^4}\frac{1}{\beta_T}\mu^2\left(\frac{\partial\mu}{\partial p}\right)_T^2 \tag{I}$$

and

$$I_{adia} = \frac{\pi^2}{2}\frac{RT}{N\lambda^4}\frac{1}{\beta_S}\mu^2\left(\frac{\partial\mu}{\partial p}\right)_S^2 \tag{II}$$

The above expressions when multiplied by the factor $\frac{6(1+\rho)}{6-7\rho}$ give the total intensity of scattered light under isothermal and adiabatic conditions.

To calculate the intensity of scattered light using expression I and II we have to obtain values of $\left(\frac{\partial\mu}{\partial p}\right)_T$ and $\left(\frac{\partial\mu}{\partial p}\right)_S$. There are two possible ways of determining these, namely (1) direct experimental evaluation of the two quantities, and (2) expressing $\frac{\partial\mu}{\partial p}$ in terms of the refractive index of the medium. By the former method Raman and Venkataraman (1939) have obtained the adiabatic piezo-optic coefficients $\frac{\partial\mu}{\partial p}$, for the first time, for a series of eleven liquids, and the isothermal piezo-optic coefficients are by Röntgen and Zehnder (1891).

For the latter the refractive index may be expressed in terms of the density of the medium in three ways:

(1) The Lorentz-Lorenz relation $\frac{\mu^2-1}{\mu^2+2} = C\rho$.

(2) Ramanathan's relation $\mu^2-1 = C\rho$.

(3) Gladstone and Dale's relation $\mu - 1 = C\rho$.

Using the above relations the intensity expression for scattered light reduces to

$$I = \frac{\pi^2}{2}\frac{RT\beta}{N\lambda^4}(\mu^2-1)^2\frac{(\mu^2+2)^2}{9}\frac{6(1+\rho)}{6-7\rho} \qquad \text{III}$$

$$I = \frac{\pi^2}{2}\frac{RT\beta}{N\lambda^4}(\mu^2-1)^2\frac{6(1+\rho)}{6-7\rho} \qquad \text{IV}$$

$$I = \frac{2\pi^2 RT}{N\lambda^4}\,\beta\,\mu^2(\mu-1)^2\frac{6(1+\rho)}{6-7\rho} \qquad \text{V}$$

In the second part of this paper, the intensities of eleven liquids, for which the adiabatic and isothermal piezo-optic coefficients are available from the work of Raman and Venkataraman (1939), and Röntgen and Zehnder (1891) are calculated using expressions I and II and compared with the values obtained experimentally. The values obtained from equations III, IV and V are also given for the sake of comparison.

Part II. Experimental

1. *The Measurement of the Relative Intensities*

For the measurement of the relative intensities of light scattered by liquids, Krishnan (1925) compared the light scattered by the liquid with the light scattered by a block of Jena glass 2 cm. thick. A parallel beam of sunlight was used as source and the comparison of intensities was effected by means of an Abney rotating sector photometer. The block of glass was then compared with a freshly prepared bulb of ether the intensity of the latter being taken as unity.

Sweiter (1927) on the other hand compared the intensity of scattered light with the source itself. A narrow parallel beam of light was partly passed through the bulb containing the liquid and partly reflected by means of suitable mirrors. The former reaches the Lummer cube directly while the latter reaches it after passing through a piece of blue glass. These two beams are then matched against each other with the help of a wedge introduced in the path of the direct light.

In the present investigation the relative intensities were determined spectroscopically. The liquids chosen were benzene, carbon disulphide, chloroform, water, methyl alcohol, ethyl alcohol, *n*–propyl alcohol, iso-propyl alcohol, *n*–butyl alcohol and iso-butyl alcohol. These liquids were distilled into the crosses several times in vacuum and sealed off. The experimental tube consisted of a pyrex glass cross constructed with tubes of 2 cm. diameter. Three of the arms were 8 cm. long, and were fused with flat ends, and the fourth arm opposite the observation end was drawn out into a horn. The walls of the crosses were painted throughout with furnace black paint leaving two apertures at right angles for the incident and scattered beams. Two of these crosses, one containing the standard liquid ethyl ether and the other, one of the liquids whose relative intensity was to be determined, were placed one on top of the other and in close contact, the two being then mounted rigidly on a wooden stand. Light from a pyrex mercury arc was focussed at the centre of these crosses by a condensing lens of aperture 18 cm. and focal length 28 cm. The incident beam was limited by two identical apertures of diameter $\frac{3}{4}$ cm. The scattered beams limited by means of a series of apertures were taken through blackened metallic tubes, diameter $\frac{1}{2}$ cm. each, and were focussed on the slit of a Fuess spectrograph by means of a large aperture short focus lens. The two spots were recorded with moderate intensity on the photographic plate so that their intensities corresponded roughly to the straight line portion of the density-log intensity curve. A series of intensity marks were taken on the same plate, with varying slit widths using as source a six volt bulb run by means of storage batteries. Density-log intensity curve was drawn for the 4358 A.U. region of the plate, and using this the ratio of the intensities were determined microphotometrically. The experiment was repeated three times and the average value was taken. The same procedure was adopted for all the liquids.

2. *Determination of the Absolute Intensity for the Standard Liquid*

To determine the absolute intensity of light scattered by the standard liquid namely ethyl ether, the light scattered transversely by it and by oxygen under 65 atmospheres pressure was photographed simultaneously under exactly identical experimental conditions. An iron cross similar to that described by Weiler (1935) was used as container for the gas, the internal diameter of which is the same as that of the pyrex glass cross containing the liquid. The internal walls of the cross were painted with spray painting. The four ends of the cross were closed by quartz windows of 1¼″ diameter and ¼″ thick, which are rendered vacuum tight by lead washers on either side of the quartz rounds. To the centre of the cross was fixed a gas adapter together with a pressure gauge capable of reading pressures accurately to 2·5 atmospheres. Pressure up to 150 atmospheres could be reached with the apparatus. The size of the incident beam was restricted by a blackened brass tubing of ½″ inner diameter inserted on one end. On the observation side a series of apertures of ⅜″ diameter were inserted so that light along the axis of the tube alone emerged out of the tube. Oxygen from a commercial cylinder was let into the tube through a plug of cotton wool to render it dust-free. A pyrex glass cross containing freshly distilled dust-free ether was placed on the top of the iron cross and its position adjusted so that the axes of illumination and observation of the two crosses were exactly one on top of the other. The distance between the two axes was 2·5″. Light from a vertical mercury arc of length 9″ was focussed by means of a large condensing lens of aperture 8″ at the centre of the two crosses. The apertures defining the sizes of the incident and the scattered beams for ether were exactly similar to those employed for the gas. The two transversely scattered beams were focussed on a photographic plate, by two identical lenses of focal length 6 cm., attached to the end of the camera. The cross and the camera were enclosed in a wooden box lined inside with black cloth. Since the scattering power of oxygen at 65 atmospheres pressure and 30° C. temperature was nearly 30 times less than that of ethyl ether, the intensity of light scattered by the latter was reduced to a suitable fraction $\left(\frac{1}{16\cdot 36}\right)$ using a rotating sector driven at constant speed by a motor, placed in front of the incident beam falling on the liquid. The ratio of the intensity of light scattered by ether to oxygen was determined microphotometrically, with the help of the density-log intensity curve for the 4046 A.U. region. The mean temperature and pressure noted was 30° C. and 65 atmospheres. The ratio obtained in the present investigation was 1·85. Since the absolute scattering power of oxygen at N.T.P. for λ 4358 A.U., was $4\cdot 31 \times 10^{-9}$, that of ether calculated from the above, after applying the necessary corrections for temperature, pressure, and the reduction of intensity was $9\cdot 4 \times 10^{-6}$. This result is in good agreement with Martin's value of $9\cdot 2 \times 10^{-6}$ at 20° C. and λ 4358 A.U.

Results and Discussion

Table I gives the relative intensities of light scattered by ten liquids with diethyl ether as standard. Columns three, four, five, six and seven give the calculated values of intensities using formulæ I, II, III, IV and V. In columns eight, nine and ten, the experimental values of intensity obtained by the author as well as those given by Krishnan (1925) and Peyrot (1936) are listed. It can be seen from the table that the relative intensities of four liquids namely benzene, carbon disulphide, chloroform and water agree well with those obtained by Krishnan. However, in the case of the alcohols the values obtained in the present investigation are found to be slightly higher than those of Krishnan. On the other hand Peyrot's data are found to be systematically lower than those of the author. This may be due to the fact that he has chosen benzene as the standard liquid. As the intensity of light scattered by benzene is five times greater than that of the alcohols, the magnitude of the error involved in the comparison of intensities will be high. The observed values for the relative intensities throughout the entire range, namely from ·21 for water to 3·1 for benzene are in fair agreement with those calculated from formula II.

TABLE I

Relative Intensities (*Ethyl ether* = 1)

Liquids	Temp. Å	I *iso*	I *adia*	I Lorentz	I Ramanathan	I G and D	I Peyrot	I Krishnan	I Author
Benzene ..	297	3·06	3·01	3·31	2·7	2·9	3·15	3·15	3·1
Carbon disulphide	295·6	12·86	12·4	13·9	9·45	11·0	..	13·0	12·8
Chloroform ..	288	1·23	1·11	1·17	1·02	1·08	..	1·26	1·25
Water ..	296·1	·19	·26	·20	·21	·20	·17	·21	·21
Methyl alcohol ..	297·4	·50	·57	·50	·51	·51	·46	..	·56
Ethyl alcohol ..	297	·61	·72	·60	·54	·60	·55	·58	·72
n-Propyl alcohol ..	297·1	·63	·72	·64	·60	·62	·57	·62	·74
Iso-propyl alcohol	298·5	·60	·75	·66	·63	·64	·53	·60	·77
n-Butyl alcohol	297·5	·68	·79	·68	·64	·65	·60	·65	·82
Iso-butyl alcohol ..	298·5	·65	·76	·66	·62	·64	..	·74	·80

Note.—G and D = Gladstone and Dale.

The absolute intensity of ether obtained by comparison with oxygen is $9{\cdot}4 \times 10^{-6}$. Assuming this value, the absolute intensities of the light scattered by the above ten liquids are calculated and given in Table II. The intensities of the transversely scattered light calculated for these liquids making use of formulæ I, II, III, IV and V are given in columns three to seven. It can be seen from the table that the observed values of the intensities for benzene, carbon disulphide, chloroform and ether are nearer the adiabatic than the

TABLE II

Absolute Intensities

Liquids	$I\times 10^6$ Author (obs.)	$I\times 10^6$ *adia*	$I\times 10^6$ *iso*	$I\times 10^6$ Lorentz	$I\times 10^6$ Ramanathan	$I\times 10^6$ G and D
Benzene ..	29	26·1	38·15	47·7	23·8	34·2
Carbon disulphide ..	120	107·4	160·4	200	83·8	128·7
Chloroform ..	11·7	9·64	15·3	16·8	9·1	12·7
Ether ..	9·4	8·6	12·5	14·3	8·8	11·6
Water ..	1·97	2·2	2·34	2·96	1·87	2·4
Methyl alcohol ..	5·3	4·9	6·3	7·1	4·6	5·9
Ethyl alcohol ..	6·8	6·2	7·6	8·7	4·8	7·0
n-Propyl alcohol ..	6·9	6·2	7·8	9·2	5·3	7·3
Iso-Propyl alcohol ..	7·2	6·5	7·4	9·4	5·6	7·5
n-Butyl alcohol ..	7·7	6·8	8·4	9·9	5·7	7·6
Iso-butyl alcohol ..	7·5	6·6	8·1	9·6	5·5	7·5

isothermal values, though they are slightly higher than the former. The same holds good for alcohols also. In the case of water the experimental value is lower than the adiabatic and isothermal ones. However, as the scattering of light by water is extremely feeble the accuracy of measurement in this case is not high. A more accurate determination of the scattering power of water by direct comparison with oxygen is in progress.

The above-mentioned facts clearly demonstrate that for all the liquids the bulk of the scattering is essentially due to an adiabatic process, and that over and above this, there is a part of scattering which should be attributed to an isothermal process.

It may be stated here that the intensities calculated from equations I and III were far too high when compared with the observed data, while equation IV yields systematically lower values. Next to equation II, equation V is found to hold good for a wide range of intensities.

In conclusion the author wishes to record her grateful thanks to Sir C. V. Raman, KT., F.R.S., N.L., for his kind interest in the work and to Dr. C. S. Venkateswaran for his helpful suggestions during the course of this investigation.

Summary

The earlier theories of the intensity of transversely scattered light by liquids have been critically examined. A general expression for the intensity of scattered light has been derived from thermodynamic principles assuming that the whole of the scattering process is (1) isothermal and (2) adiabatic. The absolute intensities of light scattered by ten liquids have been determined, first obtaining the relative intensities of these liquids taking ethyl ether as standard, and then comparing ethyl ether with oxygen at a known

temperature and pressure. The observed data of the absolute intensities of these liquids were found to be nearer the adiabatic than the isothermal values, though in general, they were slightly higher than the former. It was therefore concluded that the bulk of scattering was mainly due to an adiabatic process, the excess being attributed to an isothermal process. A comparison of the observed data with the other three formulæ derived on the assumption that the Lorentz-Lorenz's, Ramanathan's, and Gladstone and Dale's relations connecting the refractive index and the density of the medium were valid, showed that of the three, Gladstone and Dale's relation is the best representative for the liquid medium.

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INTERFEROMETRIC STUDIES OF LIGHT SCATTERING IN THE ALCOHOLS

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1. *Introduction*

When a beam of monochromatic radiation traverses a dust-free liquid, a part of the incident radiation is scattered within the fluid and emerges from it in all directions. The intensity of the light so diffused and its state of polarisation as observed in a direction transverse to the incident beam both depend to a great extent on the nature of the liquid under study. As is well known, a great part of the light so scattered owes its origin to the fluctuations of optical density within the liquid. This part of the scattering, so far as can be revealed in an ordinary spectroscope, appears as a sharply defined line in the spectrum having the same position as the incident radiation. Spectroscopic investigations of the state of polarisation of this unmodified scattering have been made by Saxena (1938) and the author (1941). These show that the transverse unmodified scattering is imperfectly polarised, and this has been ascribed to the Q-branch of the "orientation scattering" appearing superposed on the density scattering of unaltered frequency.

A closer examination of the unmodified scattering with the aid of interferometers such as the Fabry-Perot Etalon or the Lummer Plate shows it as split up into three components; one, in the position of the original frequency and the other two equally displaced from it on either side. The outer components appear to be strongly or totally polarised, while the central component is imperfectly polarised. The outer components find an explanation in the theory of Brillouin as due to sound waves of thermal origin traversing the medium. The origin of the central component however, is still a matter of speculation. In the case of the liquids in which it exhibits a high degree of depolarisation, it is evident that a part of its intensity must be ascribed to the Q-branch of the orientation scattering as already remarked. In order to obtain a further insight into its origin, it appears desirable to investigate the scattering by liquids with a low depolarisation ratio, in which case the contribution of the Q-branch to the central component may be expected to be negligible. The aliphatic alcohols satisfy this requirement, and an interferometric study of the light scattered by a series of them has therefore been undertaken and is described in the present communication.

2. *Experimental Technique*

A series of six alcohols namely, methyl, ethyl, *n*-propyl, *iso*-propyl, *n*-butyl and *iso*-butyl, as well as *iso*-amyl and allyl alcohols were chosen for the present investigation. These alcohols were distilled into the experimental tubes several times in vacuum, till they were completely dust-free, and were finally sealed off. The Wood's tubes were made of pyrex glass of 1½″ diameter with horn-shaped ends and had capacities of 400 c.c. Special care was taken to choose the tubes, since any streaks on the walls would give rise to stray scattering which is detrimental to the accuracy of the experiment. They were painted over the entire outer surface with furnace black paint leaving the front circular window clear for the purpose of illumination and observation. A Fabry-Perot etalon with a separation of 5 mm. between the plates was used for the spectral examination. The source of illumination was a zinc mercury amalgam arc, containing 15% by weight of zinc, of semicircular shape, run at 4 amps. current. Under these conditions, the zinc triplet 4680, 4722, 4810·5 A.U. had the same intensity as the 4078 A.U. radiation of the mercury arc. In order to obtain the maximum intensity for the incident light, the arc was clamped as close as possible to the circular window of the Wood's tube. The tube was surrounded by a water jacket through which water was circulated continuously to ensure constant temperature. The scattered light in the backward direction was taken through a water cooled brass tube, whose inner surface was painted black and having an aperture of 0·5 cm. diameter, and after passing through the Fabry-Perot etalon, was focussed on the slit of a Fuess spectrograph. The optical system was enclosed in a thick-walled box made of asbestos cement sheets to ensure constancy of temperature. All the alcohols were studied under identical conditions at room temperature.

To determine the ratio of the intensity of the central component to the Brillouin components, the etalon patterns were run through a Moll microphotometer, the curves for the second ring being obtained for all the alcohols. From these curves, with the help of the appropriate density-log. intensity curve, the ratios of the intensities were computed, making due allowance for the background.

3. *Results and Discussions*

The photographs in Plate XII illustrate the patterns obtained in the series of six alcohols as well as *iso*-amyl and allyl alcohols using the 4078 A.U.

radiations of the mercury arc. Fig. 2 gives the microphotometer curves for the same radiation. The ratios of the peak intensity of the central component to the sum of the two Brillouin components obtained from these curves are given in column six of Table I. Columns two to four give the temperature of investigation, isothermal compressibility β_T and adiabatic compressibility β_ϕ. It should be remarked here that these experimental values shown in column

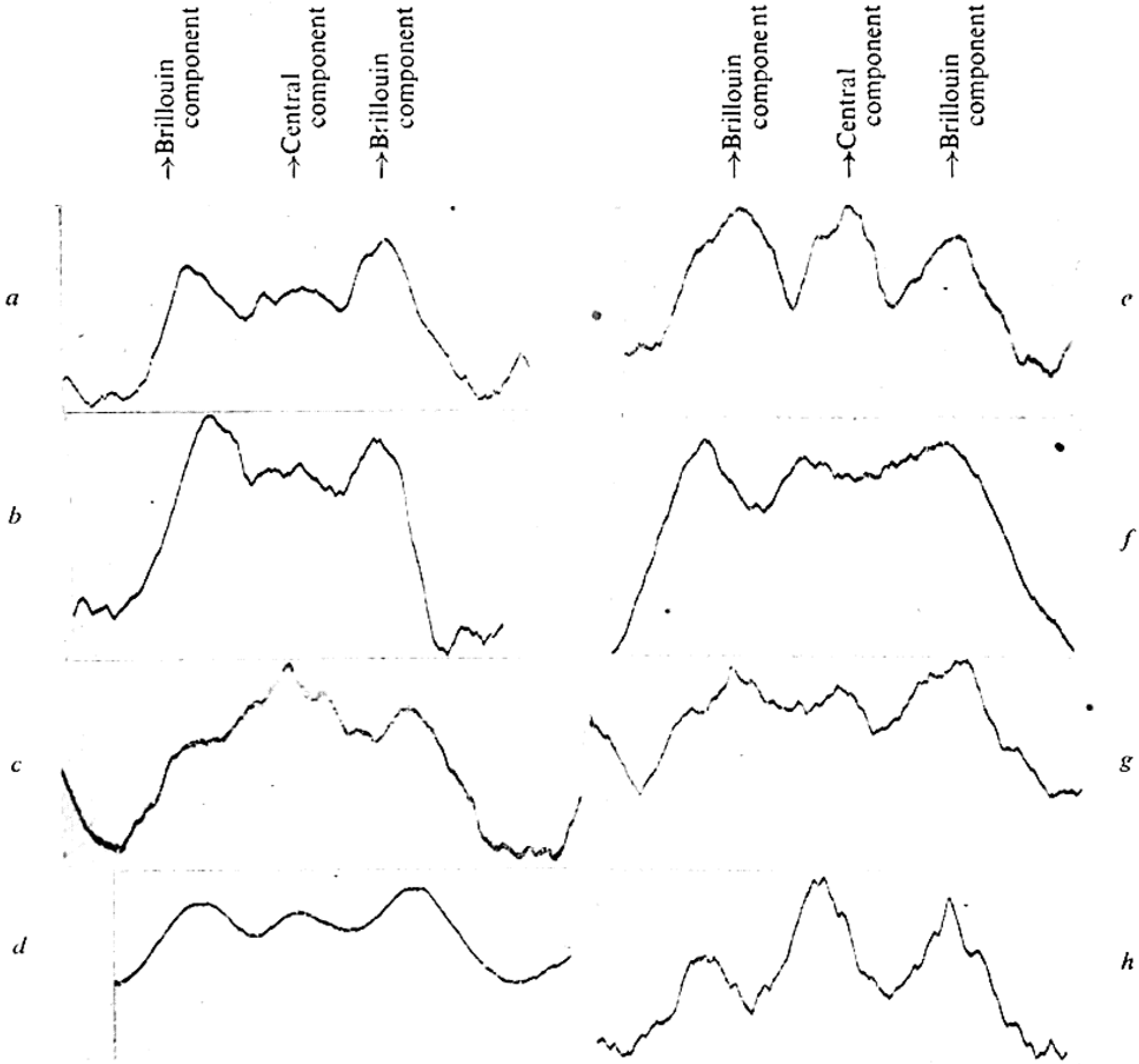

FIG. 2

Microphotometric Curves for Liquid Scattering

(*a*) Methyl alcohol.
(*b*) Ethyl alcohol.
(*c*) *n*-Propyl alcohol.
(*d*) *iso*-Propyl alcohol.
(*e*) *n*-Butyl alcohol.
(*f*) *iso*-Butyl alcohol.
(*g*) *iso*-Amyl alcohol.
(*h*) Allyl alcohol.

TABLE I

Comparison of the Relative Intensities of the Central and the Brillouin Components with the Landau-Placzek Formula

Liquids	Temp.	$\beta_T \times 10^6$	$\beta_\phi \times 10^6$	I_C/I_B calculated	I_C/I_B observed	Viscosity η 20°
Methyl alcohol .	25° C.	126·9	105·4	·205	·285	·0051
Ethyl alcohol ..	,,	115·8	97·2	·19	·375	·0168
n-Propyl alcohol ..	,,	102·2	87·2	·17	·60	·0177
Iso-Propyl alcohol ..	,,	115·9	98·3	·18	·45	·0175
n-Butyl alcohol	,,	95·4	81·8	·165	·70	·0223
Iso-Butyl alcohol ..	,,	105·0	90·6	·16	·66	·0286

six are open to three sources of error, namely (1) parasitic light reflected from the rear end of the experimental tube which will be greatest for liquids of low scattering power, (2) finite breadth of the three components and (3) the background provided by the continuum between the central and the two Brillouin components. As the intensity of scattering is the least for methyl and ethyl alcohols and the Brillouin components have then the maximum breadth, the percentage error should be expected to be the greatest in these cases. On the contrary, as may be seen from the microphotometric curves given in Fig. (2), it is just in these two cases that the central component is the weakest. This indicates that the error involved in the measurement of the relative intensities cannot be very serious.

Since the outer or Brillouin components arise from sound-waves of thermal origin traversing the liquid, the assumption that their intensities are given by the fluctuation theory in which the adiabatic compressibility is considered appears at least plausible. If it be further assumed that the total scattering by the liquid has an intensity given by the fluctuation theory using the isothermal compressibility, the difference of intensity may conceivably appear as the central or undisplaced component; the relative intensity of the central to the outer components would then be given by $(C_p - C_v)/C_v$ or by $(\beta_T - \beta_\phi)/\beta_\phi$ where C_p and C_v are the specific heats of the liquids at constant pressure and volume and β_T, β_ϕ are the isothermal and adiabatic compressibilities. Landau and Placzek (1934) have suggested that this is the case, and Birus (1938) claims to have verified the same in the cases of water, ethyl alcohol and toluene. Taking the data for isothermal and adiabatic compressibilities given by Tyrer (1914) we have calculated the ratios $(\beta_T - \beta_\phi)/\beta_\phi$ for the six alcohols. These are entered in column *five* of Table I. It can be seen that the ratio has a maximum value of 0·205 for methyl alcohol and comes down to 0·16 for *iso*-butyl alcohol. On the other hand, the present investigation gives the observed intensity ratio as 0·285 for methyl alcohol, steadily increasing for the higher members up to a maximum of 0·70 for *n*-butyl alcohol. All the observed values are much greater than the theoretical ones, showing clearly that the Landau-Placzek formula is not valid.

The Landau-Placzek formula takes no account of the possibility of the orientation or depolarised scattering by a liquid appearing as part of the unmodified scattering. The fact, that the transverse scattering by a liquid examined spectroscopically with a prismatic instrument of large dispersion and a narrow slit appears imperfectly polarised clearly shows the existence of a Q-branch or undisplaced line in the orientation scattering. The intensity of this may be obtained by multiplying the calculated intensity of the density scattering (using the isothermal compressibility) by the factor $\frac{13\rho_0}{6-7\rho_0}$, where ρ_0 is the depolarisation determined with a narrow slit. The intensity of the Q-branch thus calculated has been entered in the sixth column of Table II. Adding this to the intensity shown in the fifth column of the same table, we get the calculated intensity of the central component. Its ratio to the fourth column is entered as I_C/I_B (calculated) in the seventh column of the table.

TABLE II

Liquids	ρ_0	Calculated density scattering (isothermal)	Calculated density scattering (adiabatic)	Difference	Orientation scattering Q-branch	I_C/I_B calculated	I_C/I_B observed
Methyl alcohol	..	5·65	4·4	1·25	..	..	·285
Ethyl alcohol	·015	6·73	5·48	1·25	·22	·27	·375
n-Propyl alcohol	·03	6·87	5·45	1·42	·46	·34	·60
Iso-Propyl alcohol	·04	6·8	5·97	0·83	·62	·24	·45
n-Butyl alcohol	·06	7·12	5·76	1·36	·99	·39	·70
Iso-Butyl alcohol	·059	6·73	5·47	1·26	·92	·40	·66

The values of ρ_0 except for ethyl alcohol are taken from a paper by Ranganadham (1933) and were obtained by him using a Fuess spectrograph of a resolving power of 25,000 which is not quite adequate for such comparisons. The value for ethyl alcohol is taken from the paper by the present author in which an instrument of resolving power 75,000 was employed, ρ_0 being 0·015 instead of 0·03 as given by Ranganadham for this liquid. There is no doubt therefore that the values of ρ_0 for the other liquids should be considerably smaller than those shown in column two of Table II. It follows that the values for the orientation scattering entered in column six for all the liquids except ethyl alcohol and therefore the ratio I_C/I_B

(calculated) should be further diminished. Even without such correction, the ratio of I_C/I_B calculated is in all cases less and in some cases much less than the observed value. It is evident from the comparison with the experimental data set out in Table I and II that the suggestions of Landau and Placzek are not supported by the facts and must be regarded therefore as untenable. The basic assumption underlying the formula, namely that the total scattering is given by the isothermal fluctuation formula, also appears to be contradicted by the direct determination of the intensity of scattering made in these alcohols and described in another paper appearing earlier in this issue of the *Proceedings*. There it has been shown that the observed intensity of the polarised part of the scattering is intermediate between the values calculated on the isothermal and adiabatic postulates. The observed density scattering does in each case exhibit an excess over the value calculated on the adiabatic basis, but such excess is much less than that shown in column five of Table II and is therefore even less capable of explaining the observed intensity of the central component.

The experimental situation may thus be summarised by stating that a part of the intensity of the central component is attributable to the Q-branch of the orientation scattering in the case of the alcohols as for other liquids, but that this is only a small part of the whole. Further, while the density scattering may be in excess of that calculated for adiabatic fluctuations, such excess even when reinforced by the Q-branch is inadequate to explain the observed intensity of the central component. We are therefore obliged to interpret the experimental facts as indicating that the intensity of the Brillouin components must itself be less than that calculated on the adiabatic formula, the difference appearing in the central component. This rather remarkable conclusion becomes intelligible when the effect of viscosity on the nature of the thermal agitation in liquids is taken into consideration. The intensity ratio of the central to the outer components is observed to be greater for the higher alcohols than for the lower ones, the viscosity of the liquids being *pari passu* greater. If the viscosity of a liquid be sufficiently great, the regular propagation of sound waves in it ceases to be possible and the Brillouin components should therefore disappear. It is therefore not surprising to find that the intensity of these components as actually observed in viscous liquids is less than the full theoretical value for undamped sound wave propagation.

4. *Hypersonic Velocities in the Alcohols*

The frequency shift $\delta\nu$ of the Brillouin components is given by the relation

$\delta\nu = \pm 2 \frac{\nu}{c} \mu v \sin \theta/2$ where ν, μ, v and c are respectively the frequency of the incident radiation, refractive index of the medium, velocity of sound in the medium and velocity of light, θ being the angle between the direction of observation and incidence. The above relation indicates a method of determining the velocity of these high-frequency sound waves in the medium, if we know the frequency shift of the two Brillouin components. The frequency shift of the Doppler components of the alcohols is determined from the microphotometric curves for the 4078 A.U. radiation of the mercury arc. The velocities of the hypersonic waves in these liquids are calculated from the above relation and are listed in Table III, column five. The frequencies of the sound waves involved are between 10^8 and 10^9 per sec. The ordinary acoustic velocities calculated from the density of the medium and the adiabatic compressibilities measured by Tyrer (1914) are given in column four.

TABLE III

Liquids	Density 25° C.	$\beta_\phi \times 10^6$	Acoustic Velocity (Calc.) m./sec.	Hypersonic Velocity (Obsd.) m./sec.
Methyl alcohol ..	0·793	105·4	1093	1088
Ethyl alcohol ..	0·785	97·2	1145	1165
n-Propyl alcohol ..	0·7998	87·2	1198	1183
Iso-Propyl alcohol ..	0·780	98·3	1140	1119
n-Butyl alcohol ..	0·806	81·8	1230	1230
Iso-Butyl alcohol ..	0·798	90·6	1175	1159

It will be noticed that the figures in columns four and five are in good agreement.

5. *Observations with other Alcohols*

The Fabry-Perot patterns of two other liquids namely *iso*-amyl and allyl alcohols were also obtained in the course of the investigation. The ratios of the intensity of the central component to the two Brillouin components for these are ·43 and ·86 respectively at room temperature. The hypersonic velocities in these alcohols calculated from the Brillouin shifts are respectively 1251 and 1299 metres per sec. For lack of necessary data, these values have not been considered in the preceding discussion.

In conclusion the author expresses her grateful thanks to Sir C. V. Raman for his keen interest in the work. The author's thanks are also due to Dr. C. S. Venkateswaran for useful discussion.

Summary

The spectral character of the so-called " unmodified " light scattering by eight members of the aliphatic series of alcohols has been examined using

a Fabry-Perot etalon and a zinc-mercury amalgam lamp as the source. The intensity of the central component relatively to the outer or displaced ones is found to increase rapidly for the higher members of the series. The data are shown to be inconsistent with the suggestion of Landau and Placzek that the central component represents the difference between the optical effects of density fluctuation calculated on an isothermal and adiabatic basis respectively. The data indicate that the increase for the higher alcohols is to be correlated with their increasing viscosity which results in a transfer of an increasing proportion of the density scattering from the outer components to the central one.

The observed hypersonic velocities do not differ sensibly from the ordinary acoustic velocities for these liquids.

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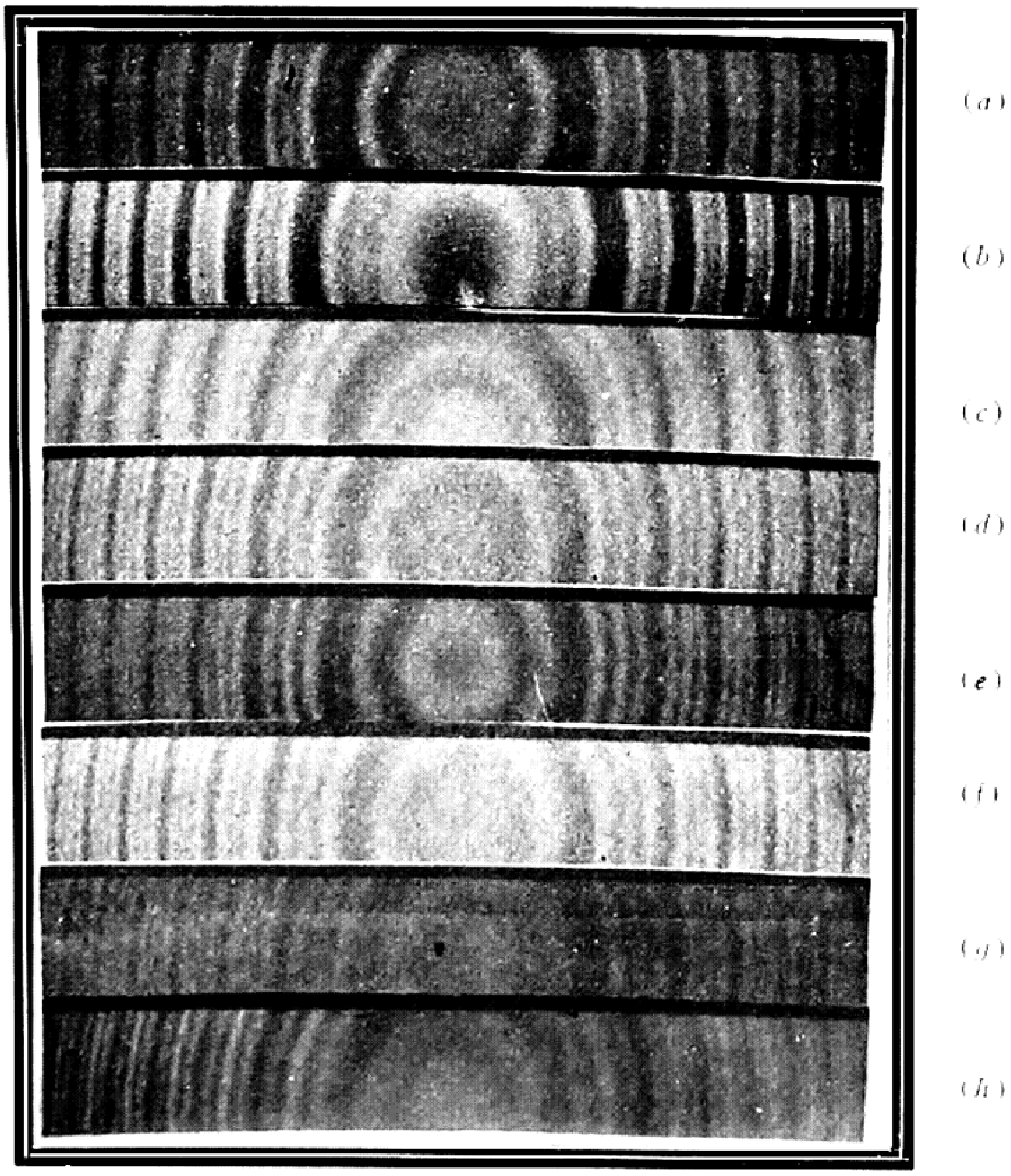

FIG. 1. Interferometric Patterns for Liquid Scattering

(*a*) Methyl alcohol
(*b*) Ethyl alcohol
(*c*) *n*-Propyl alcohol
(*d*) *Iso*-propyl alcohol
(*e*) *n* Butyl alcohol
(*f*) *Iso*-butyl alcohol
(*g*) *Iso*-amyl alcohol
(*h*) Allyl alcohol

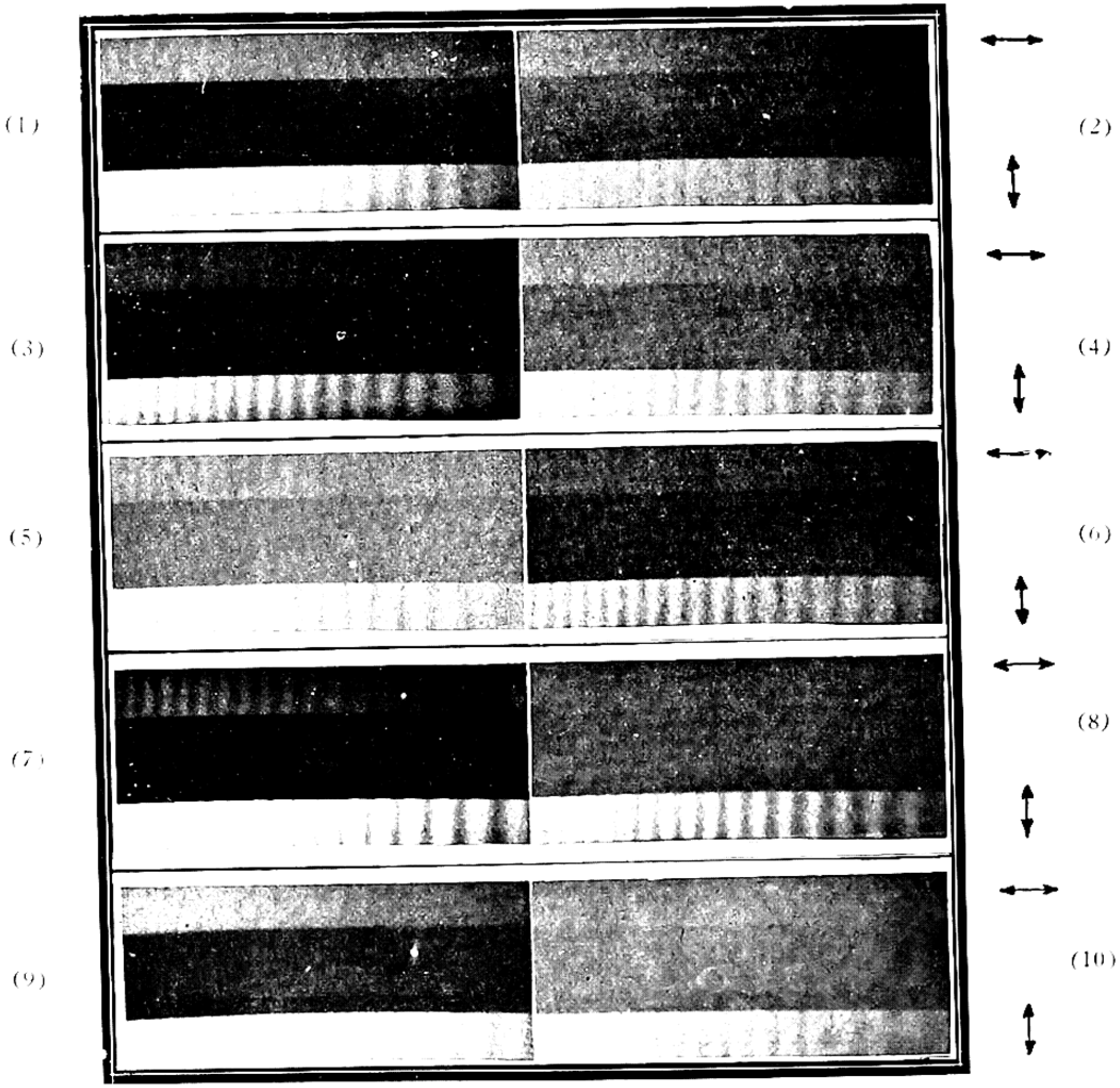

FIG. 1. Polarisation Pictures

1. Formic Acid 45° C.
2. Formic Acid 75° C.
3. Acetic Acid ,,
4. Acetic Acid ,,
5. *n*-Butyric Acid 45° C.
6. *n*-Butyric Acid 120° C.
7. *iso*-Butyric Acid ,,
8. *iso*-Butyric Acid 120° C.
9. Benzene 70° C.
10. Cyclohexanol 45° C.

INTERFEROMETRIC STUDIES OF LIGHT SCATTERING IN LIQUIDS: POLARISATION DATA

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1. Introduction

IN a previous communication the author (1941) has published the results of a detailed investigation of the spectral distribution of intensity of the anisotropic or orientation scattering of light in several liquids and its variation with temperature. The method adopted was to determine the degree of depolarisation of the transversely scattered light for slit widths varying from 2,000 μ to 10 μ. As the slit width was diminished, the depolarisation ratio decreased, evidently as the result of the exclusion of more and more of the rotational wing; from the rate of fall of depolarisation with slit width, it was concluded that irrespective of the nature of the liquid, the intensity of the depolarised rotational scattering is a maximum at the Rayleigh line itself and is distributed exponentially on either side of it. The intensity of these wings and their spectral extent are both strongly dependent on the viscosity of the liquid and its molecular anisotropy. In agreement with Saxena (1938), it was observed that in all cases the depolarisation ratio for the limiting slit width is finite and not zero as indicated by Rousset (1935). This limiting value of depolarisation was diminished by raising the temperature and consequently increasing the fluidity of the liquid.

The scope of the spectroscopic method is limited by the resolving power of the instrument employed. Indeed with a spectrograph of low resolving power, a higher limiting value of depolarisation which differs only very little from the non-spectroscopic data will be obtained. The resolving power used by the author had a value 75,000 in the 4358 A.U. region which was just sufficient to resolve lines nearly $0 \cdot 3$ cm.$^{-1}$ apart. In these circumstances, the observed limiting depolarisation is determined by the relative intensities of the fraction of the depolarised orientation scattering and of the polarised density scattering which appear with a change of frequency less than $0 \cdot 3$ cm.$^{-1}$

It is difficult to reconcile the above conclusion with the observation of Gross (1930), Rao (1934) and Birus (1937), that the central component as well as the two Brillouin components in the interferometric patterns of light scattering by liquids are completely polarised. Rao (1936) himself has, however, observed that the central components of formic and acetic acid are only partially polarised, but he attributes this to the presence of large anisotropic molecular groups in these acids. By photographing the horizontal and the vertical components in a single exposure with a Lummer plate, Venkateswaran (1942) has shown that in the cases of all liquids the central component is imperfectly polarised, the degree of imperfection depending on the depolarisation factor and on the viscosity of the liquid. In the present paper the problem is reinvestigated, with special reference to the temperature dependence of the depolarisation of the central component, in order to correlate the results with those obtained using a prismatic spectrograph.

2. *Experimental Technique*

The experimental arrangement for the measurement of the state of depolarisation of the three components was essentially the same as that given by Venkateswaran (1942) in a previous paper appearing in this number. Eight typical liquids having different degrees of depolarisation were chosen for the investigation. These liquids were repeatedly distilled in vacuum into pyrex Wood's tubes of 300 c.c. capacity, having fused-on glass ends, till they were dust-free, and sealed off. The horn of the experimental tube was painted with furnace black paint to provide a perfect dark background for scattered light. Light from a horizontal mercury arc was rendered parallel by means of a series of blackened metallic vanes arranged in succession and placed very near the tube, the convergence error for the arrangement being less than 0·1%. Light transversely scattered by the liquid was taken through a blackened metallic tube of diameter 5 mm. and focussed on the slit of a Hilger constant deviation spectroscope. A Lummer plate placed in front of the prism diffracted the rays in a vertical direction and a double-image prism placed just after the camera lens, resulted in splitting the interference pattern into the horizontal and vertical components. Due to the polarising action of the optical surfaces through which the light has to pass, the horizontal component undergoes a weakening by 12%. For investigation at higher temperatures the tube was surrounded by a mat resistance, whose temperature could be controlled by varying the current in the heating wires. The depolarisation ratio of the central component was determined microphotometrically, due allowance being made for the general background and the instrumental correction mentioned above.

3. Results and Discussion

The liquids chosen for the present investigation were formic, acetic, *n*-butyric and *iso*-butyric acids, as well as cyclohexanol, carbon disulphide, chloroform and benzene. The fatty acids were investigated both at room temperature and also at a higher temperature, while the other liquids were studied only at room temperature. These acids were specially chosen for the temperature study, because in the spectroscopic investigations carried out by the author they showed a large diminution in the limiting values of depolarisation with rise of temperature.

Fig. 1, Pl. XIII, gives typical illustrations of the Lummer patterns obtained for some of these liquids. In all the photographs, the fringes were clearly visible in the horizontal component, thereby indicating that the central component in them is partially polarised. The visibility of the fringes in the horizontal component is however markedly diminished at the higher temperatures. This indicates a fall in the intensity of the central fringe relatively to the continuous background of the pattern at higher temperatures. It is also evident from the photographs that the Brillouin components are strongly polarised. That the bright fringes in the horizontal component besides being weaker are also sharper than in the vertical component is illustrated in

TABLE I

Liquids	Prismatic Spectroscope				Lummer Plate		
	η_{20° C.	Temp. °C.	$\rho_{narrow\ slit}$	$\rho_{wide\ slit}$	Temp. °C.	ρ_{centre}	$\rho_{background}$
Formic acid	·018	30 95	·44 ·12	·53 ·45	45 75	·39 ·24	·79
Acetic acid	·012	30 110	·28 ·08	·40 ·36	45 75	·28 ·18	·74
n-Butyric acid	·0153	30	..	·36	45 120	·25 ·14	·76
Iso-Butyric acid	·0132	30 145	·15 ·06	·35 ·29	45 120	·20 ·11	·72
Cyclo-hexanol	·596	30	·066	·085	45	·06	
Carbon disulphide	·0037	20	·30	·63	45	·21	·83
Chloroform	·0056	20	·025	·175	45	·07	·74
Benzene	·0065	78	·065	·40	70	·09	·81

Fig. 2. It may be inferred that the polarisation of the Brillouin components is more nearly perfect than that of the central component.

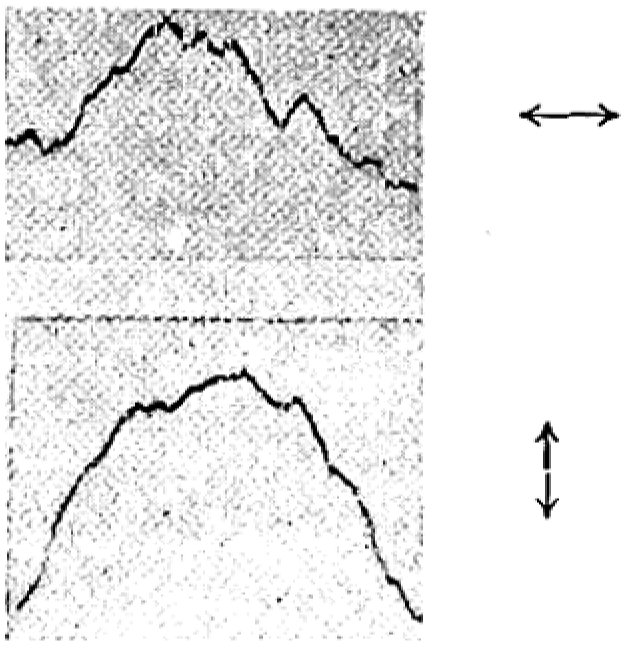

FIG. 2. Microphotometric records of horizontal and vertical components for *n*-butyric acid at room temperature.

Column seven in Table I gives the depolarisation of the central fringe in the Lummer patterns, found microphotometrically after deducting the intensity of the background in both components and allowing for the instrumental correction. The accuracy for benzene, cyclohexanol and chloroform is not great, as the horizontal component is weak for these liquids and the presence of a strong background makes the measurement difficult. For the sake of comparison, the depolarisation ratio for the same liquids obtained with a prismatic spectrograph using a broad slit as also with a very narrow slit are given in the fourth and the fifth columns of the table together with their respective temperatures of observation. It will be seen that the depolarisation of the central fringe of the Lummer pattern is roughly the same as the depolarisation of the total scattering determined spectroscopically with a narrow slit when the temperature of observation is taken into account. The polarisation of the background on the other hand approaches, though it does not quite attain, the value $\frac{6}{7}$ indicated by theory for the rotational Raman scattering.

The observation that the central component is only partially polarised for liquids is theoretically very significant. If the central component owes its origin solely to the density scattering, it should be completely polarised; if on the other hand, it were due to the Q-branch of the rotational scattering in the liquid, it should be depolarised to the extent of $\frac{6}{7}$. The partial polarisation actually observed indicates that the central component arises from both types of scattering. The fall in the intensity of the Q-branch relatively to the background at the higher temperatures observed in the Lummer patterns has evidently the same physical explanation as the rapid diminution in the values of $\rho_{narrow\ slit}$ relatively to $\rho_{wide\ slit}$ found with the prismatic spectrograph; namely that as the temperature is raised, part of the orientation scattering appearing in the Q-branch is released and appears instead in the P– and R–branches of the same. Such a phenomenon might naturally be expected in view of the noticeable diminution of viscosity at the higher temperatures and consequent increase of the freedom of the molecules to orientate themselves.

In conclusion the author wishes to record her deep sense of gratitude to Professor Sir C. V. Raman, for his interest in the work. Her sincere thanks are due to Dr. C. S. Venkateswaran for the valuable help rendered by him.

Summary

The states of polarisation of the central component and the Brillouin components in light scattering have been investigated for a series of four fatty acids and four other organic liquids using a Lummer plate. It has been observed that while the two Brillouin components are strongly polarised in transverse scattering, the central component showed a marked defect of polarisation for all the liquids. This imperfection of polarisation was found to depend on the temperature of investigation. These results are correlated with those already reached by a spectroscopic investigation of the depolarisation of light scattering in liquids.

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INTERFEROMETRIC STUDIES OF LIGHT SCATTERING IN VISCOUS LIQUIDS AND GLASSES*

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1. *Introduction*

An earlier paper appearing in the present issue of the *Proceedings* dealt with the case of mobile liquids and contained a discussion, based on the data for such liquids, of the origin of the central or undisplaced spectral component in the interferometer patterns of the light scattered by them. It emerged very clearly from these studies that the viscosity of the liquid plays a fundamental role in the appearance of this component and is the factor which principally determines its intensity relatively to the outer displaced or Brillouin components and also its state of polarisation. Accordingly, it becomes of interest to extend the study to liquids of high viscosity and to investigate how the results obtained with them are influenced by variation of temperature. The case of phenol already dealt with gives us some indication of what to expect in such cases. But the extension to liquids of great viscosity considered in the present paper has led to results which are of a somewhat unexpected character and therefore of exceptional interest.

2. *Experimental Arrangements*

The liquids studied are glycerine, castor oil, cyclohexanol and glycol as well as glucose. One of the chief difficulties in the investigations on light scattering by viscous liquids is that the ordinary method of distillation is inapplicable for rendering them free from dust and fluorescence. In the case of glycerine it is also of the utmost importance to remove all traces of water, as the presence of the latter lowers the viscosity considerably. A modified method which was found to work satisfactorily for glycerine, cyclohexanol and glycol is illustrated in Fig. 1. The liquid was first freed from water and other impurities by distilling in a reflexer and taking the middle

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* A preliminary report on the results of this investigation was made in two short notes in *Nature* (Raman and Venkateswaran, 1938, 1939).

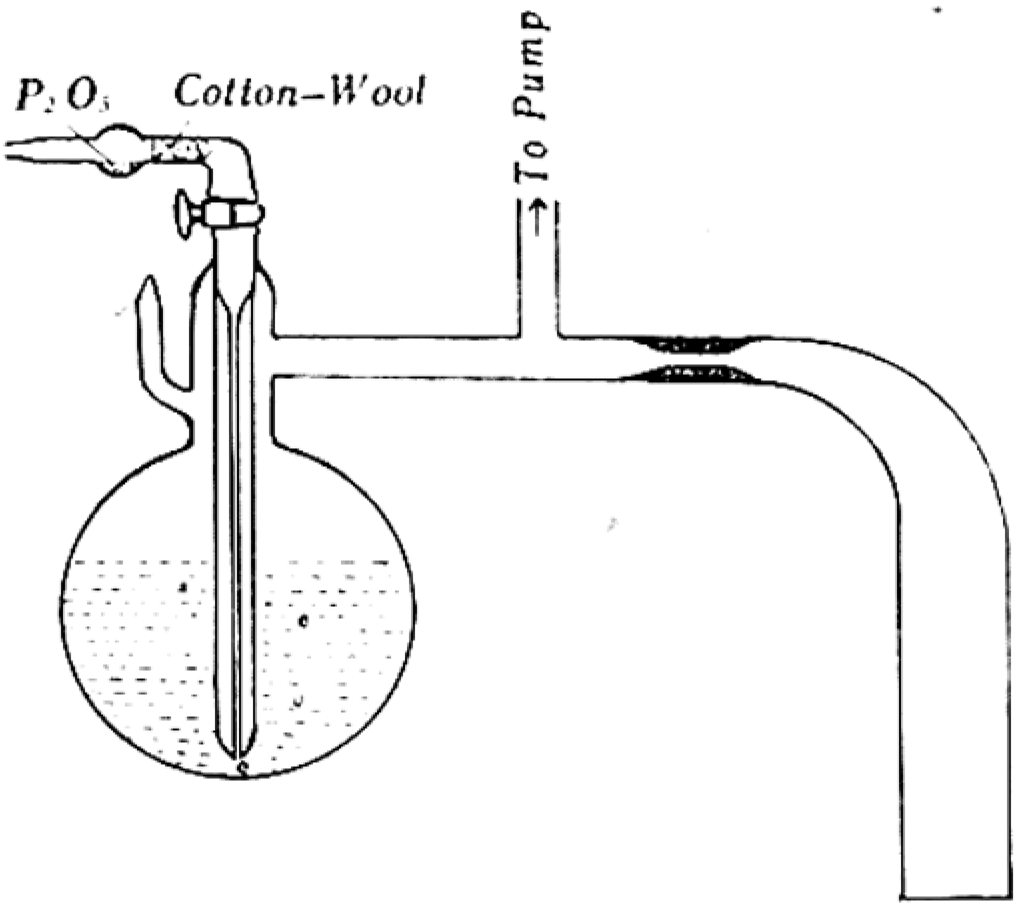

FIG. 1. Distillation Apparatus for Glycerine

fraction which distils over at a constant boiling point. The liquid was transferred through a side tube to a bulb of 500 c.c. capacity, which was connected to a Wood's tube and to a vacuum pump through a plug of cotton-wool. A small stream of air was let in through a capillary tube dipping into the liquid, which helped to avoid bumping. The liquid was heated by a carefully regulated electric heater and the first fraction of the distillate was removed by a side trap (not shown in the figure). The distillation was repeated several times and the Wood's tube filled with the liquid was finally sealed off. In the case of castor oil and glucose the substances supplied by the dealers were transferred to the tube without further purification and the air bubbles locked in the fluids removed by warming, while being connected to a pumping system. The experimental arrangement was the same as that used in the previous communications, a zinc-mercury amalgam lamp being the source of illumination. For investigating glycerine at 0° C., the tube was mounted within a metal lined wooden box, with the illumination end alone coming out through a side hole. In the case of liquids, the observations were made of the light scattered backwards; glasses were studied in the transverse setting. The plate distance for the Fabry-Perot plates was 5 mm. except in the case of the optical glass for which a 3-mm. separation was used, as the sound velocity in it is as high as 5,000 metres per second.

3. *Experimental Results*

The interference patterns obtained with the 4810 A.U. radiations of the zinc arc for all liquids included in the present investigation and for styrol glass, are given in Plate XIV. In both the organic and inorganic glasses, in spite of the fact that the interference rings are very intense, no displaced components could be observed; but a weak background overlapping the pattern is detectable. Glucose is the most viscous of the liquids studied, and no trace of the Brillouin components has been observed for it. Glycerine has been investigated at 0°, 26°, 42°, and 110° C. For all the four temperatures the spectra of glycerine are nearly of the same intensity as revealed by the intensity of the Raman line at 3,000 cm.$^{-1}$ due to the C–H group, which appears in the neighbourhood of the zinc lines. At 0° C., the Brillouin components are extremely weak. The central component is very intense; but for this temperature, it is possible that part of its intensity is due to parasitic light. At 26° C. the displaced components brighten up, though the central component still remains intense. For 4810 A.U., the positive and negative components overlap; they are just separated out in the 4622 A.U. radiations. At 42° C., they are more intense and at 110° C. their intensity is comparable to that of the central component. The Brillouin shift at 110° C. is also considerably less than at the room temperature. These changes in glycerine are analogous to those already reported for phenol, though more pronounced as we should expect from the great viscosity of the former. In castor oil, the components can be clearly seen, though they are extremely weak and difficult of reproduction in Plate XIV. With 7·5 mm. separation for the Fabry-Perot plates, the two components were found to overlap each other. In the case of glycerine, castor oil and phenol at the room temperature, the Brillouin components could not be identified in the mercury radiations, as they are overwhelmed by the hyperfine structure satellites. The negative result reported by Raman and Rao (1938) for glycerine and phenol using mercury radiations is thus not surprising. In glycol and cyclohexanol which are comparatively less viscous, the Brillouin components are very intense. Another feature which deserves special mention is that in all these liquids, the displaced components are as sharp as the incident radiation. The main features of the patterns are described in Table I. From the frequency shift $\delta\nu$ of the Brillouin components for 4722 A.U. the velocity of the thermal sound waves in these liquids is calculated using the relation $\delta\nu = 2\,\nu \cdot \frac{v}{c}\,\mu \sin \theta/2$, where ν is the frequency of the incident radiation, v and μ are the velocity of sound and the refractive index of the medium and c the velocity of light. These velocities are given in Table I along with the supersonic velocity, the temperature of observation, the viscosity and the refractive index of the liquid. The measurements for phenol are also given in the table.

TABLE I

Liquid	Temp. °C.	η in Poises	Refractive Index	Hypersonics			Ultrasonics		
				Intensity*	$\delta\nu$ in cm.$^{-1}$	Velocity m./sec.	Velocity m./sec.	Temp. °C.	Author
Glycerine ..	0	120·4	..	v.w.	..	≈2500	..	..	..
	26	9·54	1·473	w.	·51	2500	1957	28·5	Bhagavantam & Rao[1]
	42	..	1·469	med.	·50	2412	1926	40	do.
	110	..	1·456	st.	·39	1898	1840	70	do.
Castor oil ..	28	6·04	1·453	v.w.	·33	1626	1508	18	Zachoval[3]
Cyclohexanol ..	35	·203	1·465	st.	·29	1403	1442	35	Bhagavantam & Rao[1]
Ethylene glycol ..	30	·170	1·427	st.	·33	1670	1721	24	Parthasarathy[2]
Phenol ..	26	·09	1·564	v.w.	·346	1568	..	..	..
	42	·047	1·532	w.	·290	1343	..	..	..
	82	·016	1·501	med.	·265	1251	..	..	..

* v.w. = very weak, w. = weak, med. = medium intensity, st. = strong.

[1] Bhagavantam and Joga Rao, *Proc. Ind. Acad. Sci.*, A, 1939, **9**, 312.

[2] Parthasarathy, *ibid.*, 1935, **2**, 497.

[3] Zachoval, *Compt. Rend.*, 1939, **208**, 265.

4. *Significance of the Results*

The appearance of clear and well-defined Brillouin components arising from standing material waves in highly viscous liquids is very significant. According to the principles of classical hydrodynamics, plane sound waves propagated through a viscous liquid suffer a diminution of amplitude in the ratio of $\frac{1}{e}$ in traversing a number of wavelengths given by $\frac{3v\lambda}{8\pi^2\eta}$, where v is the velocity and λ the wavelength of sound, and η is the viscosity of the liquid (Lamb, *Hydrodynamics*). For 4722 A.U. radiations and at room temperature, this factor has been calculated for various liquids and entered in column six of Table II. It will be seen that except in the case of phenol, carbon tetrachloride and ether, the amplitude of the wave will be reduced to less than half its value before traversing one wavelength. In the case of glycerine and castor oil, this damping due to viscous forces is so great that we should expect that the waves would not have any physical existence. The corresponding Brillouin components should, therefore, be unobservable at room temperature. The appearance of these components thus signifies that the thermal sound waves are propagated as if the kinematic viscosity has little or no influence on them. The only effect of increased liquid viscosity is to decrease the intensity of the coherent modified scattering and enhance that of the central component. This is well illustrated by the temperature studies with phenol and glycerine.

TABLE II

$\lambda = 4722$ A.U.

Liquid	Temp. °C.	Density	Viscosity C.G.S. Units	Sound Velocity $\times 10^{-2}$ cm./sec.	$\frac{1}{e}$	$\frac{4}{3}\pi\eta/\rho\lambda$ $\times 10^{-2}$	Half-breadth in cm.$^{-1}$
Glycerine ..	26	1·26	9·54	2500	·025	13430	..
Castor oil ..	28	·96	6·04	1626	·024	11160	..
Cyclohexanol ..	35	·962	·203	1403	·640	471	·046
Glycol ..	30	1·116	·170	1670	·90	270	·027
Phenol ..	26	1·072	·090	1568	1·6	149	·016
	42	1·058	·047	1343	2·6	79	·009
	82	1·025	·016	1251	7·0	28	·003
Carbon tetrachloride	25	1·595	·008	938	10·0	·9	·001
Ethyl ether ..	30	·7135	·002	943	38·0	·5	·0005

Another point of view regarding the spectral character of scattered light has been developed by Leontowitsch (1931) by applying the method of Fourier analysis to the kinetics of fluctuations in a liquid medium. From the expression for intensity given by him it follows that two displaced components of the Brillouin type would appear in the scattered light if $\upsilon > \frac{4}{3}\frac{\pi\eta}{\rho\lambda}$, where υ and λ are the sound velocity and wavelength and η and ρ are viscosity and density of the liquid respectively. The half-breadth Δw of the components is given by $\frac{\Delta w}{w_1} = \frac{2}{3}\frac{\pi\eta}{\rho\upsilon\lambda}$, where w_1 is the frequency shift of the component. According to this theory, the displaced components would be sharper for liquids of lower viscosity and if the viscosity is so great that $\upsilon < \frac{4}{3}\frac{\pi\eta}{\rho\lambda}$, there will be no displaced components, but only a broadening of the central component. Leontowitsch himself has suggested that glycerine would provide a rigorous test of the theory. The values of $\frac{4}{3}\frac{\pi\eta}{\rho\lambda}$ as well as the half-breadth of the components are calculated for glycerine, castor oil, cyclohexanol, glycol, phenol, carbon tetrachloride and ethyl ether and given in Table II. It will be noticed that $\upsilon < \frac{4}{3}\frac{\pi\eta}{\rho\lambda}$ in the case of glycerine and castor oil and therefore the appearance of the Brillouin components and of a sharp undisplaced line in these liquids contradicts one of the main predictions of the theory. It will be seen also that the experimental observations, namely that the Brillouin components are broader for mobile liquids than for the viscous ones like glycol, cyclohexanol and phenol and that in the case of the latter, they become broader at higher temperatures are directly contrary to the conclusions indicated by the half-breadth values given in Table II.

We are thus obliged to reject the theory of light scattering put forward by Leontowitsch.

5. *The Rigidity of Liquids*

One of the striking facts of observation appearing from the present investigation is that the velocity of thermal sound waves in glycerine and castor oil at the room temperature calculated from the frequency shift of the Brillouin components is considerably higher than the ultrasonic velocity as determined for these liquids at the same temperature for longitudinal waves of frequency in the neighbourhood of 10^7 sec.$^{-1}$ generated by a piezo-electric oscillator. In the case of less viscous liquids included in Table I and several others which are dealt with in another paper appearing in these *Proceedings*, these two velocities are observed to be nearly equal. The unexpected appearance of the Brillouin components and the enhanced velocity of the thermal waves responsible for them together provide the clue for an understanding of the nature of the liquid state and liquid viscosity. According to Clerk Maxwell, the behaviour of amorphous bodies under the influence of a shearing strain is given by the equation

$\frac{ds}{dt} = \frac{1}{n}\frac{dF}{dt} + \frac{1}{\eta}F$, where s is the shearing strain; F, the corresponding stress; t, the time; n the rigidity modulus, and η the coefficient of viscosity. If the deformation is constant, $\frac{ds}{dt} = 0$ and the solution of the above equation gives $F = F_0 e^{-\frac{t}{\tau}}$, where $\tau = \frac{\eta}{n}$ is the relaxation time, that is, the time at which the stress decreases in the ratio $e:1$. In the case of periodic processes, when the period t of the external force is greater than τ, the relaxation time, the Maxwell's equation reduces to the well-known law of viscous flow for liquids, *viz.*, $\frac{ds}{dt} = \frac{F}{\eta}$. If $t \ll \tau$ it reduces to the Hooke's law, $s_2 = \frac{F}{n}$; in other words, for mechanical disturbances of sufficiently high frequency, the medium would behave practically as a rigid solid.

It is clear that if a liquid possesses the properties of a solid, the velocity of propagation of the elastic longitudinal waves would be given by $v_{solid} = \sqrt{\frac{k + \frac{4}{3}n}{\rho}}$, instead of $v_{liquid} = \sqrt{\frac{k}{\rho}}$ for an ordinary liquid, where k and ρ are the bulk modulus and the density of the medium respectively. From the fact that the velocity for ultrasonic waves of frequency of the order of 10^7 cycles per second is the same as that calculated from the adiabatic compressibility determined by static method for several liquids, we may conclude that the time of relaxation is less than 10^{-7} sec. and the fugitive rigidity of the liquid does not enter into the expression for velocity. In the case of thermal waves, the modulation frequency is given by $2\mu\,\frac{v}{\lambda}$ for backward scattering, where μ is the refractive index of the medium and λ, the wavelength of the incident light. The frequency of these waves varies from 6×10^{9} per second in CCl_4 to 10×10^{9} in castor oil and $15{\cdot}6 \times 10^{10}$ in glycerine, the corresponding time-periods being $1{\cdot}7 \times 10^{-10}$, $1{\cdot}10^{-10}$ and $\cdot 64 \times 10^{-10}$ second respectively. Since in the case of mobile liquids, *e.g.*, CCl_4, ether, etc., there is no increase in the sound velocity as we go from the ultrasonic to this *hypersonic* region, we have to assume that the time of relaxation is less than the time-period of the operative thermal waves. In glycerine at 26° C., the hypersonic velocity is nearly one-third as much more as the supersonic velocity and in castor oil also it is distinctly higher than the latter. This large increase in the velocity may be explained only by assuming that for very high frequencies, the rigidity of the liquid comes into play.

Taking the two expressions $v_{sol.} = \sqrt{\dfrac{k+\frac{4}{3}\,n}{\rho}}$ and $v_{liq.} = \sqrt{\dfrac{k}{\rho}}$ as giving the velocities of sound in the hypersonic and ultrasonic ranges of frequencies respectively, the bulk modulus and the rigidity modulus are calculated and given in Table III. The adiabatic compressibility, $\frac{1}{k}$, given by

TABLE III

Liquid.	η in Poises	Ultra-sonic Velocity	Hyper-sonic Velocity	$k \times 10^{-10}$	$n \times 10^{-10}$
Glycerine	$9{\cdot}54$	1957	2500	$4{\cdot}83$	$2{\cdot}28$
Castor oil	$6{\cdot}04$	1508	1626	$2{\cdot}18$	$\cdot 18$

Liquid	τ Time of Relaxa-tion	Time-Period of Hypersonic Waves	Calculated Adiabatic Compressi-bility	Adiabatic Compressi-bility (Observed)
Glycerine	$4{\cdot}2 \times 10^{-10}$	$\cdot 64 \times 10^{-10}$	$20{\cdot}7 \times 10^{-6}$	21×10^{-6}
Castor oil	33×10^{-10}	1×10^{-10}	$45{\cdot}9 \times 10^{-6}$	47×10^{-6}

the former agrees well with the directly observed value. The time of relaxation calculated from the viscosity and the rigidity, making use of the Maxwell's formula $\eta = n\tau$ is entered in column seven of the table, and the corresponding time-period of the hypersonic waves in column eight. In both the liquids, the time of relaxation is much larger than the actual value of the time-period of the Debye waves in the medium. With rising temperature, the divergence between the 'hypersonic' and 'ultrasonic' velocities in glycerine diminishes (see Table I), as is to be expected from the rapidly falling viscosity and the consequent fall of the relaxation time. These observations thus provide for the first time an experimental proof of the thesis that for periodic processes of very high frequencies, a liquid behaves essentially as a solid.

The question now arises whether the solid state thus revealed is crystalline or amorphous in character. In the case of crystals, the entire light scattering exhibits itself as modified components as was shown by Raman and Venkateswaran (1938) in a Note to *Nature* on their observations with gypsum. On account of the extreme difficulty of obtaining crystals free from inclusions and imperfections and in view of the fact that the phenomenon is very weak in solids, it has not been possible to obtain successful results with other crystals. That crystals, in general, give well-defined Brillouin components which are very intense compared to the central component is also shown by the observations of Sibaiya (1938) with rochelle-salt, and Gross (1940) with quartz. In the case of liquids, however, with increase of viscosity, the displaced components tend to disappear while the central component progressively gains in intensity, the patterns being then very similar to those observed for glasses. The liquid state is thus more akin to a glass than to a crystal.

The above conclusions are also supported by the observations that the rotational wings on either side of the Rayleigh line appearing in the spectra of light scattered by liquids are very weak in highly viscous liquids. In Fig. 2, Plate XIV, the spectra of a series of seven liquids taken with a narrow slit and a high dispersion spectrograph are reproduced. It will be seen that in spite of the fact that ρ, the depolarisation of glycerine, is as high as $\cdot 33$, the 'wings' are almost completely absent as in the case of glasses, while they are a prominent feature of mobile liquids, *e.g.*, chloroform, toluene and benzene. In formic acid ($\rho = \cdot 53$) for which the viscosity lies between these two extremes, the wing possesses only a moderate intensity.

In conclusion, the author desires to place on record his heartfelt thanks to Prof. Sir C. V. Raman for his keen interest in the work.

Summary

In an interferometric study of light scattering by highly viscous liquids, sharp and well-defined Brillouin components have been recorded for glycerine and castor oil. The intensity of these components in glycerine shows a

progressive increase as the temperature is raised from 0° to 110° C., the central undisplaced component indicating a corresponding diminution in intensity. The Brillouin components appear with great intensity in cyclohexanol and glycol which are relatively less viscous. On the other hand, no displaced components are observed in glucose and in styrol and optical glasses. While the velocity of the thermal sound waves calculated from the Brillouin displacement agrees well with the supersonic velocity in cyclohexanol and glycol, it is considerably higher than the latter in glycerine and castor oil. The divergence between the 'hypersonic' and the 'ultrasonic' velocities diminishes as the temperature of glycerine is raised to 110° C. The appearance of well-defined Brillouin components in these highly viscous liquids indicates that the ordinary laws of hydrodynamics are not valid for the propagation of these high frequency waves in the medium. The results are also shown to be in contradiction to the predictions made by the theory of light scattering in liquids put forward by Leontowitsch. From the ultrasonic and hypersonic velocities in glycerine and castor oil, the bulk modulus, k, and the rigidity modulus, n, have been determined. The time of relaxation τ calculated using the Maxwell's formula $\eta = n\tau$ where η is the viscosity, is in both cases greater than the time-period of the thermal sound waves, thereby furnishing an experimental proof of the thesis that the liquid behaves essentially as an amorphous solid at sufficiently high frequencies. These conclusions are also supported by observations on the dependence of the intensity of the rotational 'wing' on the viscosity of the liquid.

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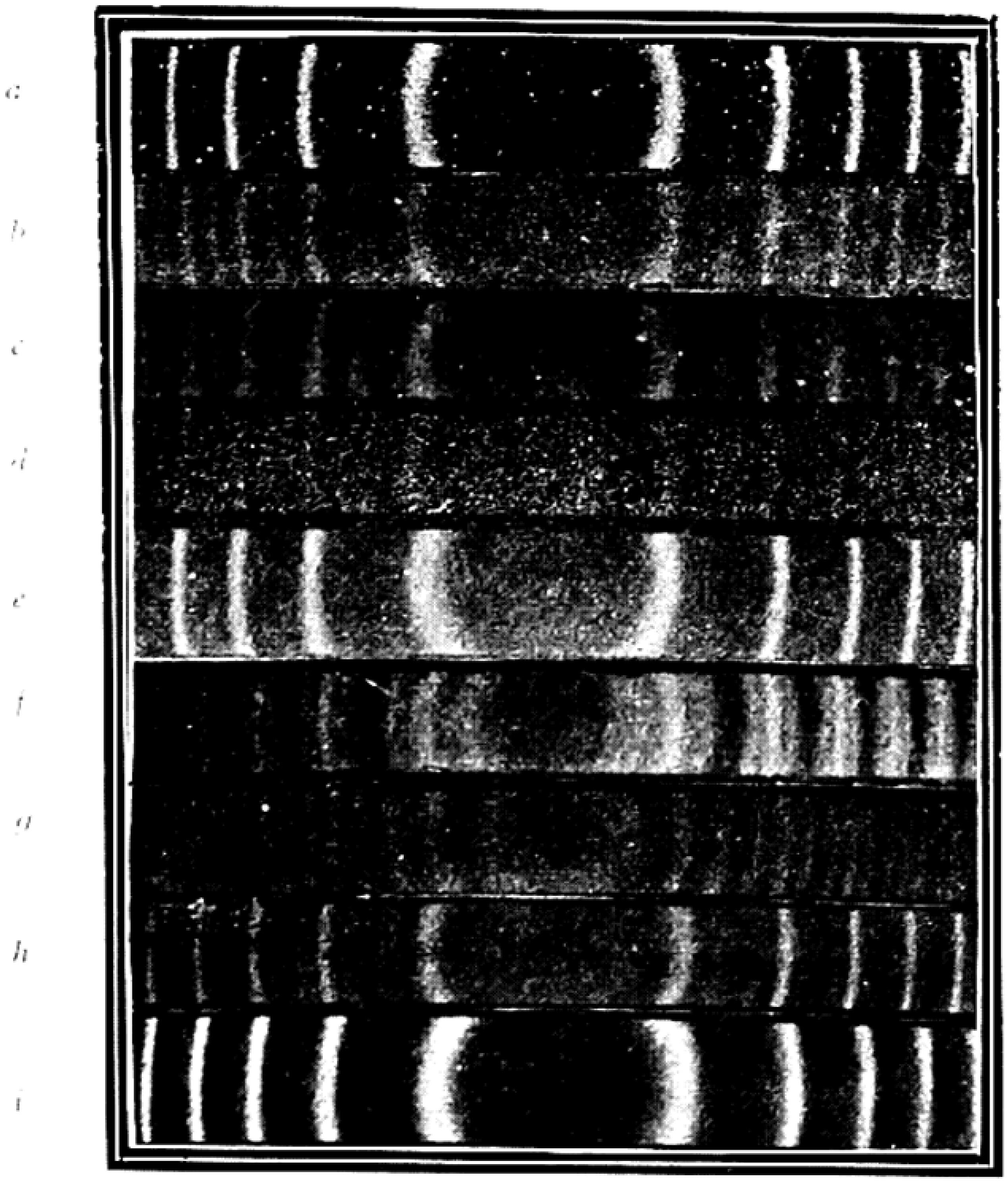

Fig. 2

Interferometer Patterns

(a) Glycerine (0° C.), (b) Glycerine (26° C.)
(c) Glycerine (42° C.), (d) Glycerine (110° C.)
(e) Castor Oil, (f) Cyclohexanol
(g) Glycol, (h) Phenol
(i) Styrol glass

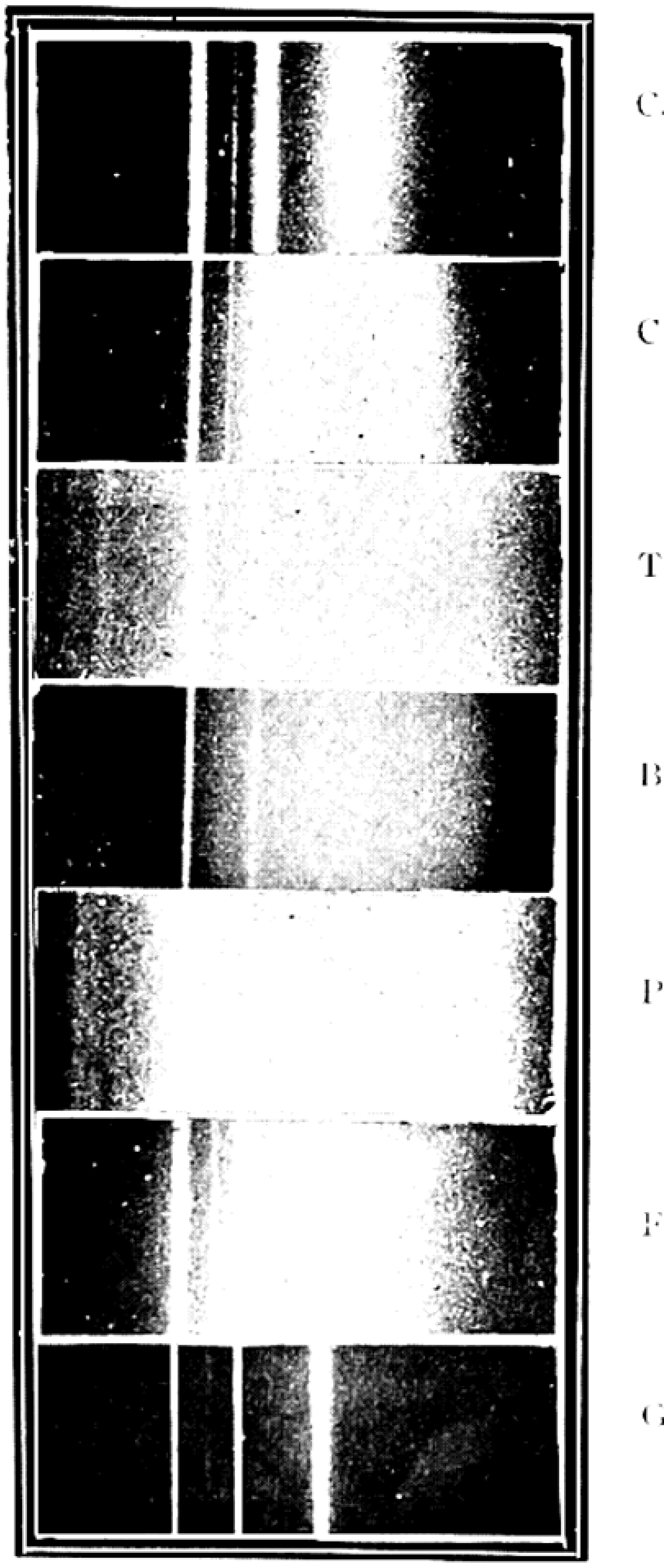

Fig. 3
Rotation Wings in Liquids

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INTERFEROMETRIC STUDIES OF LIGHT SCATTERING : HYPERSONIC VELOCITIES IN LIQUIDS

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1. *Introduction*

One of the outstanding problems connected with the liquid state is the anomalous absorption of sound waves observed at the range of ultrasonic frequencies. Varied suggestions have been put forward (see Bergmann, 1938) to explain the phenomenon; but the one which demands the first consideration is that due to Kneser (1938). According to him, the abnormal increase of the absorption coefficient at high frequencies, which, in some cases, like benzene and chloroform, is about hundred-fold as much as is to be expected from classical considerations, is due to the lowering of the effective specific heat in a manner analogous to what is established for gases for the rapid periodic processes involved in ultrasonics. This would lead to a dispersion of sound velocity in the liquids in the frequency region at which the absorption coefficient shows the maximum anomaly. Numerous papers* have appeared in recent years dealing with this aspect of the problem by the ultrasonic method. The maximum frequency so far attained by the piezo-electric method is less than 10^8 per second, and the increase of sound velocity over the value obtained in the audible region may be expected to be only 1% of the latter. Due to experimental difficulties such as the inconstancy of temperature and variation of the frequency of the oscillator, the measurements of ultrasonic velocities so far obtained have not been able to give a decisive answer to the question, beyond indicating that the dispersion, if at all it exists, is small in the region studied.

Interferometric analysis of the spectral character of the " unmodified " light scattering in liquids provides a method of determining the acoustic velocities in liquids at a frequency of 10^{10} cycles per second, which is 100–1000 times higher than the frequency range employed in the ultrasonic investigations. According to Kneser's theory, the velocity reaches its upper limiting value at high frequencies, estimated by him to be of the order of 10^9 Hertz. Accordingly the velocity calculated from the Brillouin displacements in light scattering should be the maximum possible and be systematically higher than the ordinary sound velocity. The percentage increase over the normal value would lie between 10–30% depending on the liquid and should, therefore, be detectable by the interferometric methods.

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* For references see Bär, *Proc. Ind. Acad. Sci.*, 1938, **8**, 289; Parthasarathy, *ibid.*, 1935, **2**, 497; Richardson, *Proc. Phys. Soc.*, 1940, **52**, 480; Krishnan, K. G., *Proc. Ind. Acad. Sci.*, 1939, **9**, 382.

2. *Experimental Methods*

The accuracy of measurements of the velocity of thermal sound waves in liquids from the frequency shifts of the Brillouin components, depends on using a highly monochromatic incident radiation and maintaining a constant temperature for the liquid under investigation and for the optical system. As mentioned in the earlier papers in this *series*, the latter conditions were secured by surrounding the experimental tube by a water jacket and by enclosing the interferometer and the spectroscope in an asbestos-cement casing. The maximum temperature fluctuation in the liquid was about 5° C. The source used was a mercury-zinc amalgam lamp run at a comparatively low current. The zinc radiations were fairly sharp and the Brillouin components were in most cases well defined. The error due to the angular width of the incident beam is negligible in the backward scattering. Frequency shifts of the displaced components were ascertained for the zinc line, 4722 A.U. and for the mercury radiation, 4078 A.U. for which the hyperfine structure satellites are extremely weak. The separation of the Fabry-Perot plates was ordinarily 5 mm.; a larger separation of 7·5 mm. was employed for liquids like ethyl ether, carbon tetrachloride and chloroform for which the frequency shifts are small. The displacements were measured by a Hilger cross-slide microscope and in cases where the shifts are not great, they were also estimated from the microphotometric curves taken at a magnification of eighty. Considering the breadth of the Brillouin and the central components the error of measurement should be taken to be as high as ± 25 metres per second. The percentage accuracy is, however, much greater in the case of liquids like water, glycol, etc., for which the displacement is large and the components are sharp.

3. *Results and Discussion*

Seventeen liquids representative of a wide range of physical properties such as viscosity, conductivity and sound absorption are chosen for the investigation. Table I gives the 'hypersonic' velocities in these liquids, calculated from the measured shifts $\delta\nu$ for the 4078 and 4722 A.U., using

TABLE I. *Acoustic Velocities in Liquids*

Liquid	Hypersonics						Supersonics				
	Mean Temp. ° C.	Refractive Index H_γ	$\delta\nu$ cm.$^{-1}$ for 4078	Velocity m./sec.	$\delta\nu$ cm.$^{-1}$ for 4722	Velocity m./sec.	Temp. ° C.	Velocity m./sec.	Author*	Velocity (Parthasarathy)	Temp. ° C.
Acetone	28	1·364	·254	**1139**	·213	**1129**	28	**1153**	Z.	1203	22·5
Carbon tetrachloride ..	25	1·484	·226	**932**	·195	**938**	23	925	F.H.A.	**929**	23
Chloroform	30	1·450	·229	**966**	·198	**980**	25	**995**	W.	1001	23·5
Cyclohexane	30	1·434	·285	**1201**	·245	**1234**	31·5	**1205**	S.	1257	23
Cyclohexanol	35	1·471	·340	**1414**	·290	**1428**	35	**1442**	B. & R.	1622	23·5
Ethyl ether	30	1·362	·210	**943**	..	..	30	**949**	F.H.A.	..	..
Ethyl alcohol	25	1·365	·261	**1169**	·220	**1166**	25	**1150**	W.	1207	23·5
Ethylene glycol	30	1·427	·390	**1661**	·333	**1670**	..	..	..	**1721**	24
Benzene	28	1·524	·32	**1290**	·268	**1281**	31·5	**1275**	S.	1310	23
Tetralin	30	1·546	·352	**1390**	·304	**1420**	..	..	..	**1465**	24
Phenol	26	1·564	..	..	·346	1568	..	..	..	..	..
Formic acid	25	1·378	·30	1331	·250	1312	..	..	..	..	..
Acetic acid	25	1·386	·257	**1139**	·22	**1153**	26	**1144**	K.	..	..
Iso-butyric acid	28	1·402	·257	1123	·21	1132	..	..	..	..	..
Methyl acetate	28	1·363	·255	**1144**	..	..	28	**1140**	Z.	1211	24
Water	30	1·343	·33	**1518**	·285	**1509**	23	**1492**	B.	1494	24
Conc. KBr solution (700 gm. in 1000 c.c. water)	28	1·38	..	..	·30	**1568**	18	**1570**	Sp.	..	..

* Z. = Zachoval (1939)
W. = Willard (1941)
S. = Suryaprakasa Rao (1940)
B.R. = Bhagavantam and Joga Rao (1939)
F.H.A. = Feyer, Hubbard and Andrews (1929)
K. = Krishnan, K. G. (1941)
Sp. = Spakovskij (1938)
B. = Bär (1938)

the Brillouin's formula $\delta\nu = 2\nu . \frac{v}{c} . \mu \sin \theta/2$, where v and μ are the sound velocity and refractive index of the medium, c is the velocity of light and $\theta = 180°$ for longitudinal scattering. The mean temperature of observation and the refractive index for H_γ are also listed for all liquids. The index used for calculation is corrected for the wavelength used. The velocities determined by the ultrasonic method are entered in columns nine and eleven for comparison. It will be seen that the hypersonic velocities calculated from the shifts for 4078 and 4722 A.U. agree fairly well, within the limits of experimental error.

In comparing the hypersonic and the ultrasonic velocities, it should be borne in mind that the liquids used for light scattering are freshly distilled and kept in vacuum during exposure, whereas it is not clear from the literature, whether sufficient care has been taken by the investigators in ultrasonics to maintain the liquid in a pure state. However, making due allowance for the temperature variation of velocities, the values obtained in the present investigation do not appreciably *exceed* the corresponding ultrasonic velocity in any liquid. Kneser's theory of sound absorption and dispersion of velocity cannot thus be sustained by the experimental facts for the case of liquids. The velocity data obtained by both the methods are *nearly* equal in the case of all liquids given in Table I. The small difference that is observed has to be attributed to the errors of measurement and the slight variations of temperature in the liquids and do not necessitate any special mechanism to be postulated.

The data published by Parthasarathy (1935) are consistently higher than those obtained by subsequent workers. The author is unable to confirm the great divergence between the hypersonic and the ultrasonic velocities reported by Rao (1938) for carbon tetrachloride and acetone. It is probable that the measurements of Rao are vitiated by the hyperfine structure satellites of the mercury radiations and by the uncertainty of the temperature of observation.

Among the liquids studied, water deserves special mention. Ever since Dutta (1938) reported a small dispersion for it, several authors have reinvestigated the liquid with different frequencies. By taking special precautions to eliminate all sources of error, Bär (1939) has been able to demonstrate that the sound velocity for water has a constant value for a wide range of ultrasonic frequencies. As the Brillouin components are sharp and well-separated from the central line, the percentage error in the determination of the hypersonic velocity in water is relatively small.

The observed value for the hypersonic region agrees well with the ultrasonic velocity duly corrected for the differences of temperature. Among the other liquids, Spakovskij (1938) claims that acetic acid shows a slight increase of velocity by about 1% in going from the frequency range of 250 kc./sec., to 2500 kc./sec. A similar dispersion for this acid is also reported by Krishnan (1941). The hypersonic velocity for the acid, however, has nearly the same value as that reported by Krishnan for 7618 kc./sec. Concentrated KBr solution also gives a value which is nearly the same as obtained by Spakovskij for 270–290 kc./sec., thus indicating that there is no dispersion in the case of electrolytic solutions as well.

In conclusion, the author's thanks are due to his Professor Sir C. V. Raman, F.R.S., for his kind interest in the work.

Summary

The 'hypersonic' velocities for eighteen representative liquids are calculated from the Brillouin displacements in the light scattered by these liquids. The data are compared with those obtained by the ultrasonic method. No detectable dispersion of velocity has been observed in any liquid in going over from the frequency range of 10 MHz in the ultrasonic to 10000 MHz in the hypersonic region.

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ANALYSIS OF THE RAMAN SPECTRUM OF SINGLE CRYSTALS OF NAPHTHALENE

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1. *Introduction*

In a previous communication to these *Proceedings*, the author[1] (1941) has reported some preliminary studies on the Raman spectra of single crystals of naphthalene. In the present communication a more detailed and exhaustive study is reported. Spectra have been obtained in which the orientation of the crystal with respect to the directions of incidence and observation have been varied, as also the states of polarisation of the incident and scattered radiations. As the structure of the naphthalene crystal is known, it has been found possible from these studies to infer with some confidence the character of the oscillations which give rise to the Raman lines, especially those with low frequency shifts. While the work was in progress, an interesting paper by Hilmi Benel[2] (1940) on the same subject has appeared. References to this work will be made in the course of the present paper.

2. *Some Experimental Details*

A specially clear and large crystal was prepared for the purpose from the melt by the method previously described. The crystal was cut in the form of a rectangular parallelopiped $2 \times 1 \times 1$ cms. in size with its edges along the axes α, β and γ of the optical polarisability ellipsoid. The polished faces of the crystal were attached to microscope cover slips by the method of fusion, and the corners were bound up to avoid volatilisation. The experimental arrangements to record the spectra were the same as have been described in some of the earlier papers of the author. A large-aperture Ahrens prism of calcite served to polarise the incident light. A double-image prism placed just in front of the slit of the spectrograph served to split up the scattered light into its horizontal and vertical components. The study was carried out with a Hilger two-prism spectrograph having a dispersion of approximately 28 Å/mm. in the λ 4358 region.

3. *Results*

As has been remarked in an earlier paper by the author[3] (Nedungadi, 1941) in the case of biaxial crystals belonging to the orthorhombic, monoclinic and triclinic classes, we may obtain 24 different spectrograms corresponding to six possible settings of the crystals and two possible directions of vibration for each of the incident and scattered radiations. All these 24 spectrograms have been recorded and reproduced for naphthalene in Figs. 1 to 12 in Plate **XV**. The orientation of the optical directions* α, β and γ as well as the state of polarisation of the incident and scattered light are indicated alongside the spectra. The Raman lines with small frequency shifts recorded by λ 4047 Å of the mercury arc are particularly clear and instructive and hence, these are also reproduced in Figs. 13 to 24 in Plate **XVI**.

As is usual in such studies, the light is assumed to be incident along OX and the scattered light observed along OY, OZ being perpendicular to both (respectively represented by →, ↑ , ○ in the Figs.). Spectra were also obtained with incident light unpolarised and scattered light analysed for the above orientations of the crystal, but these have not been reproduced. In most cases a comparison iron arc was recorded alongside of each of the two components of the spectrum so as to enable small displacements, if any, relative to each other of the lines in the differently polarised components to be detected. Though the author has reported 28 internal and 4 lattice oscillations in the earlier paper, the polarisation behaviour of the extremely feeble lines among these could not be recorded in the present case, as exposures long enough to bring up these lines would obliterate the polarisation data of the more intense lines by over-exposure. Though the various spectra recorded were under similar conditions, these might not have been exactly identical in view of the long exposures that had to be given. Hence, great accuracy in the relative intensities of the Raman lines in different spectrograms recorded on separate photographic plates is not claimed. The relative intensities are recorded, the most intense line in any pair of spectrograms being assigned a value 15. The polarisation characters of the various Raman lines for all the orientations studied are recorded in Table I.

4. *Theoretical Considerations*

The normal modes of vibration of a free molecule are determined by its symmetry and by the forces holding the atoms together. When such a molecule forms part of a crystal lattice, we should expect new modes of oscillation

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* α, β and γ respectively indicate the directions of minimum, intermediate and maximum refractive indices of the crystal.

TABLE I

$$\text{Depolarisation}—\rho = \frac{\textit{Intensity of the horizontal component } OX}{\textit{Intensity of the vertical component } OZ}$$

	Orientation of the Crystal	Incident Light	38	47	75	107	121	389	463	512	764	1021	1143	1169	1242	1384	1463	1576	3058
1	α—OX	Polarised // to OZ	$\frac{0}{0}$	$\frac{0}{5}$	$\frac{13}{3}$	$\frac{5}{0}$	$\frac{0}{0}$	$\frac{1}{0}$	..	$\frac{1}{8}$	$\frac{1}{5}$	$\frac{0}{4}$	$\frac{1}{0}$	..	..	$\frac{2}{15}$	$\frac{0}{4}$	$\frac{1}{1}$	$\frac{1}{5}$
	β—OY	,, // to OY	$\frac{7}{10}$	$\frac{0}{0}$	$\frac{8}{15}$	$\frac{0}{0}$	$\frac{10}{0}$	..	..	$\frac{0}{6}$	$\frac{1}{2}$	$\frac{0}{2}$	$\frac{0}{1}$	..	$\frac{0}{1}$	$\frac{5}{8}$	$\frac{0}{2}$	$\frac{1}{2}$	$\frac{2}{3}$
	γ—OZ		..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..
2	α—OX	Unpolarised	..	..	$\frac{15}{5}$	$\frac{2}{6}$	$\frac{3}{1}$	$\frac{1}{0}$	..	$\frac{1}{3}$	$\frac{1}{5}$	$\frac{0}{2}$	$\frac{2}{1}$	$\frac{0}{1}$	$\frac{0}{1}$	$\frac{3}{9}$	..	$\frac{2}{4}$	$\frac{3}{4}$
	β—OZ	Polarised // to OZ	$\frac{7}{0}$	$\frac{0}{5}$	$\frac{7}{5}$	$\frac{1}{15}$	$\frac{14}{1}$	..	$\frac{0}{1}$	$\frac{1}{2}$	$\frac{3}{12}$	$\frac{1}{3}$	..	..	..	$\frac{4}{15}$	..	$\frac{3}{8}$	$\frac{4}{7}$
	γ—OY	,, // to OY	$\frac{0}{6}$	$\frac{0}{0}$	$\frac{15}{7}$	$\frac{5}{1}$	$\frac{0}{0}$	$\frac{1}{0}$	..	$\frac{2}{2}$	$\frac{1}{2}$	$\frac{1}{1}$	$\frac{1}{1}$	..	..	$\frac{1}{3}$	..	$\frac{1}{2}$	$\frac{2}{2}$
3	α—OY	Unpolarised	..	..	$\frac{9}{12}$	$\frac{1}{3}$	$\frac{7}{0}$	$\frac{1}{1}$	$\frac{0}{1}$	$\frac{3}{10}$	$\frac{3}{9}$	$\frac{2}{8}$	$\frac{2}{1}$	$\frac{1}{0}$	$\frac{0}{1}$	$\frac{5}{15}$	$\frac{1}{6}$	$\frac{4}{1}$	$\frac{4}{7}$
	β—OX	Polarised // to OZ	$\frac{5}{0}$	$\frac{0}{5}$	$\frac{7}{1}$	$\frac{1}{0}$	..	..	..	$\frac{2}{5}$	$\frac{1}{4}$	$\frac{1}{3}$	..	..	..	$\frac{4}{15}$	$\frac{0}{3}$	$\frac{2}{1}$	$\frac{2}{4}$
	γ—OZ	,, // to OY	$\frac{4}{0}$	$\frac{0}{0}$	$\frac{2}{15}$	$\frac{0}{3}$	$\frac{5}{0}$	..	..	$\frac{0}{1}$	$\frac{1}{0}$	..	$\frac{0}{1}$	..	..	$\frac{2}{1}$	..	$\frac{1}{0}$	$\frac{1}{1}$
4	α—OY	Unpolarised	..	..	$\frac{12}{3}$	$\frac{7}{3}$	$\frac{5}{0}$	$\frac{2}{0}$	$\frac{0}{1}$	$\frac{8}{2}$	$\frac{2}{12}$	$\frac{2}{2}$	$\frac{3}{0}$	$\frac{1}{0}$	..	$\frac{7}{15}$	$\frac{2}{0}$	$\frac{1}{9}$	$\frac{3}{8}$
	β—OZ	Polarised // to OZ	$\frac{8}{0}$	$\frac{0}{4}$	$\frac{8}{3}$	$\frac{0}{15}$	$\frac{0}{0}$	..	$\frac{0}{1}$	$\frac{2}{1}$	$\frac{0}{10}$	$\frac{0}{2}$	$\frac{1}{0}$	$\frac{1}{0}$	..	$\frac{2}{13}$	..	$\frac{1}{6}$	$\frac{1}{5}$
	γ—OX	,, // to OY	$\frac{0}{3}$	$\frac{0}{0}$	$\frac{15}{2}$	$\frac{3}{0}$	$\frac{0}{5}$	$\frac{1}{0}$	..	$\frac{1}{0}$	$\frac{0}{1}$	..	$\frac{2}{0}$	..	..	$\frac{1}{2}$	..	$\frac{0}{2}$	$\frac{1}{2}$
5	α—OZ	Unpolarised	..	..	$\frac{8}{15}$	$\frac{1}{9}$	$\frac{6}{1}$	..	..	$\frac{2}{2}$	$\frac{2}{2}$	$\frac{1}{1}$	$\frac{1}{1}$	..	..	$\frac{5}{4}$	..	$\frac{3}{2}$	$\frac{4}{4}$
	β—OX	Polarised // to OZ	$\frac{7}{0}$	$\frac{0}{0}$	$\frac{4}{8}$	$\frac{1}{15}$	$\frac{8}{1}$	..	..	$\frac{1}{1}$	$\frac{4}{5}$	..	$\frac{0}{1}$	..	..	$\frac{6}{4}$	..	$\frac{3}{3}$	$\frac{4}{4}$
	γ—OY	,, // to OY	$\frac{7}{0}$	$\frac{0}{0}$	$\frac{9}{15}$	$\frac{2}{4}$	$\frac{1}{1}$	$\frac{1}{1}$	..	$\frac{4}{2}$	$\frac{3}{1}$	$\frac{1}{1}$	$\frac{1}{1}$	$\frac{1}{0}$	$\frac{1}{0}$	$\frac{6}{3}$	$\frac{1}{0}$	$\frac{8}{0}$	$\frac{4}{4}$
6	α—OZ	Unpolarised	..	..	$\frac{15}{2}$	$\frac{1}{7}$	$\frac{0}{5}$	$\frac{1}{0}$	..	$\frac{4}{1}$	$\frac{2}{5}$	$\frac{1}{2}$	$\frac{2}{0}$	..	$\frac{1}{0}$	$\frac{5}{7}$	..	$\frac{1}{3}$	$\frac{2}{4}$
	β—OY	Polarised // to OZ	$\frac{0}{0}$	$\frac{0}{0}$	$\frac{15}{2}$	$\frac{2}{14}$	$\frac{0}{0}$	$\frac{1}{0}$	..	$\frac{2}{1}$	$\frac{1}{6}$	$\frac{1}{8}$	$\frac{1}{0}$	..	..	$\frac{3}{4}$	..	$\frac{1}{2}$	$\frac{1}{4}$
	γ—OX	,, // to OY	$\frac{7}{5}$	$\frac{0}{0}$	$\frac{15}{3}$	$\frac{0}{0}$	$\frac{0}{13}$	$\frac{1}{0}$	..	$\frac{5}{0}$	$\frac{3}{3}$	$\frac{2}{0}$	$\frac{2}{0}$	$\frac{1}{0}$	..	$\frac{5}{4}$	..	$\frac{2}{3}$	$\frac{4}{4}$
Depolarisation in the melt			..	..	..	..	..	D	..	·65	·50	·55	·77	..	D	·34	·64	·85	·55

to arise corresponding to the rotational and translational degrees of freedom of the molecule. In the case of aromatic crystals like naphthalene, the frequencies of such oscillations would be determined by the weak Van der Waal's forces that hold the crystal together and hence, they must be expected to have low values. Indeed, in most of the organic crystals the corresponding lines in the spectra are contained within a frequency shift of about 130 cm.$^{-1}$ from the exciting line. We shall call these the lattice oscillations in the sense that they do not occur in the vapour or liquid but only in the solid state. For an interpretation of the experimental data given earlier in this paper, we have to consider what the symmetry of the molecule and of the crystal have to tell us regarding the normal modes which give rise to the various lines appearing in the spectra.

It has been, now, fairly well established that the naphthalene molecule consists of two fused benzene rings and has a plane structure with symmetry D_{2h}. Bonino[1] (1936) and Saxena[5] (1938) have given the number and symmetry of the normal modes of the molecule from group theoretical considerations. The relevant data taken from their character table are given in Table II.

TABLE II

D_{2h}	Total number of modes n_i	Translations and Rotations	No. of vibrations of the molecule n_i'	No. of vibrations of the ring	Selection Rules	
					Raman	Infra-red
A_1	9	0	9	5	*p*-pol.	*f*
A_2	9	R_{wz}	8	4	*p*-dep.	*f*
B_1	4	R_{wy}	3	1	*p*-dep.	*f*
B_2	5	R_{wx}	4	2	*p*-dep.	*f*
A_1'	4	0	4	2	*f*	*f*
A_2'	5	Q_z	4	2	*f*	*p*
B_1'	9	Q_y	8	4	*f*	*p*
B_2'	9	Q_x	8	4	*f*	*p*

It can be seen from the table that there are 48 modes of vibration of the molecule distributed among eight classes, out of which 24 are active in the Raman effect, 20 in infra-red and 4 inactive in both. Further, as the molecule has a centre of symmetry, there is no coincidence between the Raman and infra-red active modes. Among the Raman active oscillations, 9 should be polarised and the rest depolarised in the spectra of the liquid and the vapour. Further, it is to be remarked that there are 17 planar oscillations for the molecule which are confined to the classes A_1 and A_2 in this table.

Like many other aromatic crystals, naphthalene crystallises in the monoclinic prismatic class with the space group C^5_{2h}. The molecular orientations in the crystal as derived from X-ray and magnetic studies have already been described in the previous paper of the author. The unit cell contains two molecules. The elements of symmetry for the crystal are (1) Identity E, (2) One two fold screw axis C_2, (3) Centre of inversion i and (4) Glide plane reflection σ_h. The full character table together with other relevant features are given in Table III.

TABLE III

C^5_{2h}	E	C_2	i	σh	n_i	T	External		n_i' $C_{10}H_8$	n_i' Ring	Selection Rules	
							T′	R′			Raman	Infra-red
A_1	1	1	1	1	27	0	0	3	24	12	*p*	*f*
A_2	1	−1	1	−1	27	0	0	3	24	12	*p*	*f*
B_1	1	1	−1	−1	27	1	2	0	24	12	*f*	*p*
B_2	1	−1	−1	1	27	2	1	0	24	12	*f*	*p*
ω_R	36	0	0	0								
$hj\chi_j'$	108	0	0	0								
$hj\psi_j'$	96	0	0	0								

In this table n_i and n_i' have the same meaning as in Table II, T represents pure translation of the lattice as a whole, while T′ and R′ give the number of translatory and rotatory modes inside the lattice; *p* and *f* indicate whether the oscillation is permitted or forbidden. It must be mentioned here that the above details regarding the lattice oscillations have been previously considered by Bhagavantam[6] in a recent paper (1941), reference to which may be made for the method of separating out the rotational and translational degrees of freedom under T, T′ and R′.

It may be readily seen from the table that all the translatory oscillations in the crystal are forbidden in Raman effect, while all the 6 rotatory oscillations are permitted. Out of the active ones, 3 belonging to class A_1 are due to rotatory oscillations of the two molecules which are symmetric to all the elements of symmetry of the crystal lattice. The three modes in class A_2 correspond to similar oscillations of the two molecules which are antisymmetric to C_2 and σ_h.

As regards the internal modes we find that there should be really 48 Raman active oscillations in the crystal, 24 of which should be totally symmetric with respect to all the elements of symmetry of the crystal and the rest antisymmetric to some of them. A comparison of Tables II and III shows that effectively the 24 Raman active molecular oscillations contained in the four classes are now confined to one totally symmetric class in the crystal. Each of these further splits up into a symmetric component belonging to class A_1 and an antisymmetric component to class A_2. The four modes in class A_1' of the molecule (Table II) forbidden both in Raman effect and infra-red absorption have obviously changed into infra-red active oscillations in the crystal. As in the case of the molecule, there should not be any coincidence between the Raman and infra-red active frequencies in the crystal also.

The polarisation studies carried out with a single crystal as have been done in the present case, immediately enable us to identify the symmetric and antisymmetric oscillations from among the Raman active modes seen in Table III. The selection rules for the appearance or otherwise of the Raman lines in such studies can be deduced geometrically by considering the deformations in the ellipsoid of optical polarisability produced by the particular vibration. The vibrations of a crystal will possess in general the same properties of symmetry as those of the point group characteristic of the crystal. Hence, considerations of the form of the polarisability figure and the symmetries of the particular vibration enable one to get the vanishing components of the polarisability tensor. The general form of the deformation of the polarisability figure is an elongation along the three axes and rotations about the three axes. The equation for the deformed ellipsoid will involve six components of the change of polarisability tensor namely $\epsilon_{\alpha\alpha}$, $\epsilon_{\beta\beta}$, $\epsilon_{\gamma\gamma}$, $\epsilon_{\alpha\beta}$, $\epsilon_{\beta\gamma}$ and $\epsilon_{\alpha\gamma}$. If all these components are zero, then that particular oscillation is forbidden in Raman effect.

All the vibrations of a monoclinic crystal can be divided into two types (1) symmetric and (2) antisymmetric. During symmetric oscillations the axes of the deformed ellipsoid continue to remain as the axes of symmetry. However, in a monoclinic crystal there is only one axis of symmetry β which remains as the principal axis of the deformed ellipsoid and the axes α and γ are no longer axes of symmetry. Hence, for such oscillations $\epsilon_{\alpha\gamma}$ will not be zero. Thus the tensor components which should vanish for symmetrical oscillations are $\epsilon_{\alpha\beta} = \epsilon_{\beta\gamma} = 0$. Similar considerations will show that for antisymmetric oscillations $\epsilon_{\alpha\alpha} = \epsilon_{\beta\beta} = \epsilon_{\gamma\gamma} = \epsilon_{\alpha\gamma} = 0$, the magnitudes of the surviving components in both the above cases depending upon the particular mode concerned. These selection rules give the characteristic tensor for a symmetric oscillation as

$$\begin{vmatrix} \epsilon_{\alpha\alpha} & 0 & \epsilon_{\alpha\gamma} \\ 0 & \epsilon_{\beta\beta} & 0 \\ \epsilon_{\gamma\alpha} & 0 & \epsilon_{\gamma\gamma} \end{vmatrix}$$

and for an antisymmetric oscillation as

$$\begin{vmatrix} 0 & \epsilon_{\alpha\beta} & 0 \\ \epsilon_{\beta\alpha} & 0 & \epsilon_{\beta\gamma} \\ 0 & \epsilon_{\gamma\beta} & 0 \end{vmatrix}$$

5. *Lattice or External Oscillations*

Let us now examine our experimental results and ascertain how far they agree with the foregoing considerations. Experimentally, four lattice lines with frequency shifts 45, 75, 107 and 121 cm.$^{-1}$ have been reported previously for the naphthalene crystal. The present detailed studies have revealed the existence of really six separate lattice lines which can be grouped into three pairs, in complete agreement with theoretical expectation. The lowest lattice line reported previously as 45 cm.$^{-1}$ is found actually to consist of two separate lines with frequency shifts 38 and 47. These two could be separated out clearly in spite of their inherent breadth, because, the polarisation characters are totally different for the two lines. The second group similarly consists of two lines with shifts 72 and 78 cm.$^{-1}$ It should be remarked here that the differential behaviour of the two lines 72 and 78 could not be clearly observed since they were not resolved sufficiently. However, that there are two lines in the diffuse band has become clear from a close scrutiny of the various spectrograms. It may be expected that if the spectrum is recorded at liquid air temperature it will show up the two lines separately. The third group consists of the two lines 107 and 121 as has already been observed. The values of these frequency shifts and their great intensities further support the theoretical finding that these are all due to rotational oscillations involving the movement of the highly anisotropic molecules and are not due to their translatory movements, in which case, the corresponding lines should be much feebler and of lower frequency.

Again, according to the selection rules of the polarisability theory, when the symmetry axis β of the crystal is set along the direction of observation OY, the antisymmetric oscillations should disappear when the electric vibrations of the incident light are along OZ. Table I and Figs. 1 and 11 show that the lines 38, 121 and apparently 72 also disappear in both the components. These three lines can therefore be taken as the three oscillations belonging to class A_1 in the character table. On the other hand for the same orientation of the crystal, if the incident light vector is parallel to OY, all the symmetric oscillations should disappear. This is found exactly to be the case with the lines 47, 107 and probably 78 also in Figs. 2 and 12. The kind of distinction indicated above between the symmetric and antisymmetric oscillations could be made out in every one of the 24 spectrograms reproduced as Figs. 1 to 12. Particularly striking examples are those of Figs. 3 and 7 where the symmetric oscillations appear only in the vertical component and the antisymmetric ones only in the horizontal component of the analysed spectra. From a close consideration of all the spectrograms the following characteristic tensors are derived for the various oscillations.

Line 38

$$\begin{vmatrix} 0 & m & 0 \\ m & 0 & s \\ 0 & s & 0 \end{vmatrix}$$

Line 47

$$\begin{vmatrix} 0 & 0 & 0 \\ 0 & m & 0 \\ 0 & 0 & m \end{vmatrix}$$

Doublet at 75

$$\begin{vmatrix} m & w & s \\ w & w & m \\ s & m & 0 \end{vmatrix}$$

Line 107

$$\begin{vmatrix} s & 0 & w \\ 0 & s & 0 \\ w & 0 & 0 \end{vmatrix}$$

Line 121

$$\begin{vmatrix} 0 & m & 0 \\ m & 0 & 0 \\ 0 & 0 & 0 \end{vmatrix}$$

In the above, *f* indicates that the component is faint, *w*–weak, *m*–medium and *s*–strong.

It is easily seen that the tensor for the doublet at 75 can be split up into two, one symmetric and another antisymmetric corresponding to the lines 78 and 72 respectively. The tensor for the other lines also agree very well with the general form given in the last section for symmetric or antisymmetric oscillation as the case may be. It is noteworthy that for the symmetric oscillation 78 and 107, $\epsilon_{\gamma\gamma}$ is also zero or extremely weak while for the line 47, $\epsilon_{\alpha\alpha}$ and $\epsilon_{\alpha\gamma}$ are both zero or negligibly small. Similarly, the antisymmetric oscillation corresponding to the line 121 has $\epsilon_{\beta\gamma} \approx 0$. These are due to the fact that the magnitudes of the polarisability terms involved during these oscillations are extremely small.

Having separated out the symmetric and antisymmetric components of the lattice oscillations, it remains to identify the respective axes about which the molecules execute the rotational oscillations. The problem cannot be fully solved as we are ignorant of the crystalline force fields which must influence the geometric modes of such oscillations. Nevertheless, some inferences may be drawn with due reservations, from a consideration of the intensities of the observed lines and their frequency shifts. We may expect the frequency shift to depend to a great extent upon the moment of inertia involved in a particular oscillation. The intensity, on the other hand, would depend upon the optical anisotropy coming into play during that oscillation. As a rough approximation, we may assume that the molecular plane is parallel to the $\beta\gamma$ plane in the crystal. The rotational oscillation about the normal to the molecular plane involves the maximum moment of inertia, and hence, the lowest pair of frequency shifts 38 and 47 may reasonably be assigned to such an oscillation. This is supported by the comparatively low intensity of these lines in view of the very low optical anisotropy in the molecular plane (Sundararajan,[7] 1939) involved in such motion. Oscillations about the breadth of the molecule involves the maximum anisotropy and an intermediate value for the moment of inertia and hence the intense lines 72 and 78 might correspond to these oscillations. The lines 107 and 121 might then be due to oscillations about the length of the molecule, as the moment of inertia about this axis is a minimum and the optical anisotropy involved has an intermediate value.

At this stage it will be useful to consider what light the present conclusions throw on the question of the origin of these low frequency lines in the crystal in relation to the 'wings' in the liquid state. Raman and Krishnan[8] (1928) originally put forward the idea that the 'wings' in the liquid arise from the impeded rotations of the molecules which are not sufficiently resolved to be recorded as separate Raman lines, its intensity being determined by the optical anisotropy of the molecules. However, Gross and Vuks[9] (1935) came forward with the view that as the low frequency lattice lines in many organic crystals fall in the region where the 'wings' in the liquid appear, the latter are completely made up of these lattice lines which become diffuse and merge with one another. This explanation assumes, without adequate justification, a persistence of the crystal lattice in the liquid state. In the case of naphthalene—and the same should be the case with all aromatic crystals belonging to the monoclinic class—it has been proved in the present paper that these low frequency lines are entirely due to the angular oscillations of the molecule about three mutually perpendicular directions in the crystal. When the crystal melts to form the liquid, it is clear that these rotational oscillations of the molecules would tend to pass over into hindered rotations due to the release of the crystalline forces. This shows that the fundamental explanation of Raman and Krishnan remains essentially true.

6. *Internal oscillations*

A comparison of the spectra of naphthalene in the solid and liquid states shows that generally, the shifts in the frequencies of these internal oscillations due to change of state are not conspicuous in many cases. This is obviously due to the fact that the weak crystalline forces do not strikingly disturb the strong interatomic valence forces of the molecule involved in such oscillations. However, the symmetry of the oscillations need no longer depend upon the symmetry of the molecule, but will be determined by that of the crystal. Oscillations symmetric with respect to the elements of symmetry of the molecule may not generally be symmetric to the elements of symmetry of the crystal. Hence, information regarding the symmetric oscillations of naphthalene molecule occurring in class A_1 of Table II may with advantage be derived from polarisation studies of the substance in the molten or vapour states. Nevertheless, as the molecules have fixed orientations in the crystal, studies on single crystals enable one to differentiate the planar oscillations of the molecule from the perpendicular ones.

Attention has already been drawn in the previous paper of the author to the striking effects of the optical anisotropy of the naphthalene molecule on the intensities with which its planar oscillations appear in the spectra. This effect is remarkably demonstrated also by the series of spectrograms reproduced in Figs. 1 to 12. It will be seen that when the crystal is set such that either of the axes γ or β lies along OZ and if the incident light also vibrates along this direction, many of the internal planar oscillations are very intense (see Figs. 1 to 8). This is due to the fact that these directions are roughly parallel respectively to the length and breadth of the molecule in the lattice. On the contrary, the very same lines are comparatively much feebler if α is set in the above manner, as this axis is roughly normal to the molecular plane along which its optical polarisability is a minimum. From the behaviour of these lines indicated above, it can be concluded with some confidence that the lines 512, 764, 1021, 1143, 1242, 1384, 1442, 1463, 1576 and 3058 correspond to some of the 17 planar oscillations of the molecule. Further, amongst these, the lines 512, 764, 1021, 1384, 1463 and 3058 appear polarised in the spectrum of the melt and consequently, these give 5 among the 9 oscillations belonging to the totally symmetric class A_1 of the molecule. The remaining lines 1143, 1242, 1442 and 1576 which are depolarised in the liquid, therefore belong to the class A_2.

It should be mentioned in passing, that the present polarisation studies have confirmed the existence of a line 463 reported hitherto only by the present author as its polarisation behaviour is slightly different from that of the line 512 as seen in case 4 of Table I. This avoids the former line being mistaken for the line 512 excited by λ 4348 of the mercury arc, as has been obviously done by earlier workers.

Let us now examine the polarisation data of these internal oscillations in order to find out how far their behaviour is governed by the conditions of crystal symmetry. In this connection, mention should be made of the detailed study of the polarisation of fluorescence and of the Raman spectrum in naphthalene crystal by Hilmi Benel (1940) who has recorded the spectra of the scattered light for all the possible orientations of the crystal as has been done in the present case. Though the low frequency lattice oscillations have been left out of study, this author has derived the characteristic tensors for about 7 internal oscillations from their observed intensities in the various spectra. This author concludes from the observed results that the polarisability theory does not hold good in respect of these internal oscillations. We shall consider this question in the light of our experimental results.

From an evaluation of the intensities of the lines in various spectrograms the following characteristic tensors are derived.

$$\begin{array}{cccc}
\mathbf{512} & \mathbf{764} & 1021 & 1384 \\
\begin{vmatrix} f & 0 & f \\ 0 & f & m \\ f & m & m \end{vmatrix} &
\begin{vmatrix} m & f & 0 \\ f & s & 0 \\ 0 & f & w \end{vmatrix} &
\begin{vmatrix} 0 & f & f \\ f & w & f \\ f & f & w \end{vmatrix} &
\begin{vmatrix} w & w & f \\ w & s & w \\ f & w & s \end{vmatrix} \\
\mathbf{1463} & \mathbf{1576} & \mathbf{3050} & 389 \\
\begin{vmatrix} 0 & 0 & 0 \\ 0 & 0 & m \\ 0 & m & s \end{vmatrix} &
\begin{vmatrix} m & f & 0 \\ f & s & f \\ 0 & f & f \end{vmatrix} &
\begin{vmatrix} m & m & 0 \\ m & s & f \\ 0 & f & s \end{vmatrix} &
\begin{vmatrix} 0 & 0 & w \\ 0 & 0 & f \\ w & f & 0 \end{vmatrix} \\
\mathbf{463} & \mathbf{1143} & 1169 & 1242 \\
\begin{vmatrix} 0 & 0 & 0 \\ 0 & f & 0 \\ 0 & 0 & f \end{vmatrix} &
\begin{vmatrix} f & 0 & w \\ 0 & 0 & f \\ w & f & 0 \end{vmatrix} &
\begin{vmatrix} 0 & 0 & 0 \\ 0 & 0 & f \\ 0 & f & 0 \end{vmatrix} &
\begin{vmatrix} 0 & 0 & f \\ 0 & 0 & w \\ f & w & 0 \end{vmatrix}
\end{array}$$

It will be observed many of the above tensors are not strictly characteristic of the symmetric or the antisymmetric type of oscillation but are due to combinations of the two. This should evidently be due to the fact that they have really a complex structure, *i.e.*, that they consist of at least two oscillations, one belonging to the symmetric and another to the antisymmetric type as is to be expected. We should, indeed, expect such a splitting of the lines in the crystal due to the fact that the intermolecular forces influence the symmetric and antisymmetric oscillations differently. A careful scrutiny of the various spectrograms was therefore carried out to detect such splitting of the lines, if any, by looking for relative shifts between the horizontal and vertical components in each figure and also by comparing the positions of the component lines with the iron arc lines recorded in superposition with them. Such a splitting has been clearly detected at least in the case of the two lines 512 and 1576. The line 512 is seen split up into a line due to an oscillation of the symmetric type having a higher frequency occurring in the vertical component and another of lower frequency of the antisymmetric type with a strong surviving tensor component $\epsilon_{\beta\gamma}$ in the horizontal (observed in Figs. 5, 7 and 10). In the case of the line 1576, the higher frequency component is due to an antisymmetric oscillation, while the lower frequency one is due to a symmetric oscillation as can be clearly detected in Fig. 3. Measurements made on the negatives of Figs. 9, 10, 11 and 12 have also confirmed the splitting of this line. The difference in frequency shifts between the split components for both the lines 512 and 1576 is only about 4 to 5 wave-numbers. It is further found that for both these lines the symmetric component occurs in those components of the spectra in which anyone of the terms $\epsilon_{\alpha\alpha}$, $\epsilon_{\beta\beta}$, $\epsilon_{\gamma\gamma}$ or $\epsilon_{\alpha\gamma}$ would appear, and the antisymmetric component occurs where the terms $\epsilon_{\beta\alpha}$ or $\epsilon_{\gamma\beta}$ are effective. Some of the spectrograms give indications of similar splitting of the lines 1384 and 3058 also. This effect appears, thus, to be a general feature of the internal oscillations, the separation between the split components in many cases, however, being too small to be detected. Thus it can be concluded that the internal oscillations can also be classified as either symmetric or antisymmetric in accordance with the requirements of the monoclinic symmetry of the crystal. The observed deviation from the theoretically expected behaviour of these lines recorded by Hilmi Benel is only a consequence of the failure to take this splitting into consideration.

The number of internal oscillations corresponding to the lines appearing in the spectrum of the melt and of the crystal may now be examined in detail in respect of their agreement with the theoretical deductions, given in Section 4. For this purpose, the frequency shifts observed in the crystal by the author and in the melt recorded by Saxena (1938) are given in Table IV. As the presence of lines with frequency shifts 191, 1406 and 3244 reported by Saxena appears to be very doubtful, they have been left out of the following discussion.

TABLE IV

No.	Raman lines		No.	Raman lines	
	Melt	Single crystal		Melt	Single crystal
1	397 (1) D	389 (2)	13	1239 (1) D	1242 (2)
2	"	463 (1)	14	1257 (2) D	1258 (½) 1280 (2)
3	511 (6) P	512 (10)	15	1326 (1) P	1324 (½)
4	726 (1) D	724 (1)	16	1379 (15) P	1384 (15)
5	760 (6) P	764 (13)	17	1438 (2) D	1442 (1)
6	772 (1) P	784 (1)	18	1460 (4) P	1463 (3)
7	941 (2) P	948 (1)	19	1530 (0) D	1519 (0) 1537 (½)
8	"	972 (½)	20	1576 (5) D	1576 (7)
9	1024 (5) P	1021 (6)	21	"	1624 (1)
10	1142 (2) D	1102 (½) 1143 (3)	22	"	3000 (1) 3026 (½)
11	"	1169 (2)	23	3058 (4) P	3058 (8)
12	1206 (0) D	1215 (½)	24	"	3086 (½)

A perusal of the table shows that as many as 28 Raman lines have been recorded in the case of the crystal, while only 18 have so far been reported in the spectrum of the melt. This is, indeed, due to the great intensity of the spectrum recorded for the crystal in comparison with that for the melt. A close consideration of these frequency shifts enables one, as has been indicated in the table, to fix up the frequencies of the 24 Raman active fundamental modes of the molecule required by theory. The apparent coincidences with the infra-red of four of the crystal frequencies mentioned by the author in the earlier paper may be purely accidental, as no such coincidence is expected from theory. It is probable that the pairs of lines marked in the table as the fundamentals 10, 14, 19 and 22 arise from a Fermi splitting due to accidental degeneracy. Thus

764 + 389 = 1153, which lies in the region of the doublet 1102–1143
764 + 512 = 1276 ,, ,, ,, 1258–1280
1021 + 512 = 1533 ,, ,, ,, 1519–1537
1576 + 1438 = 3014 ,, ,, ,, 3000–3026

We may also expect that the 6 frequencies listed as 2, 8, 11, 21, 22, 24 in the table, as also the missing components arising from the Fermi-splitting, will be observed in a spectrum of the melt if recorded with sufficiently long exposure. Each one of these 24 fundamentals may further be expected to split up under high resolution into a symmetric and an antisymmetric component in the crystal as has been indicated from the polarisation studies.

Comparing the magnitudes of the frequency shifts in the solid and liquid states, one finds that there are deviations amounting even up to about 10 wavenumbers accompanying the change of state for some of the fundamentals such as 1, 6 and 12 of the table, whereas there is absolutely no such change for some of them, *e.g.*, 20 and 23. It may, however, be seen that, broadly, there is a tendency for the frequency shifts to be higher in the crystal than in the melt. Large differences of the intensities of the corresponding lines in the two states are also noticed in the table in some cases. It would be premature to discuss the significance of these features until their reality has been confirmed by more exact studies. From this point of view, further investigations of the spectra of naphthalene in the liquid and in the crystal recorded side by side with a Hartmann diaphragm on the same photographic plate and using a spectrograph having higher dispersion are desirable.

In conclusion, the author wishes to express his sincere thanks to Prof. Sir C. V. Raman for his continued encouragement during the progress of this work.

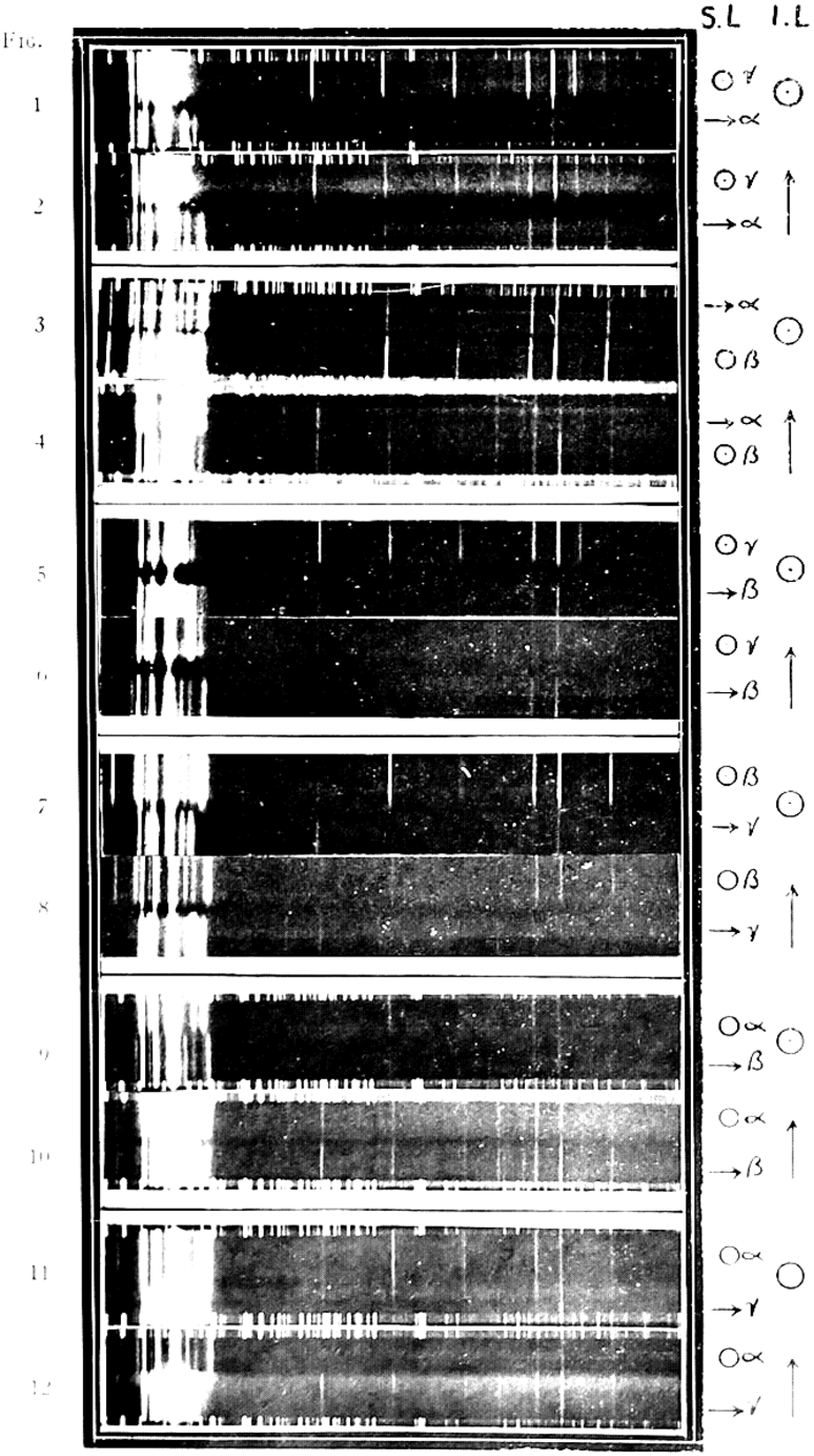
Fig.
1
2
3
4
5
6
7
8
9
10
11
12
S.L
I.L
⊙ γ
→ α
⊙
⊙ γ
→ α
↑
→ α
⊙ β
⊙
→ α
⊙ β
↑
⊙ γ
→ β
⊙
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⊙ α
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→ β
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→ γ
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→ γ
↑

[illegible]

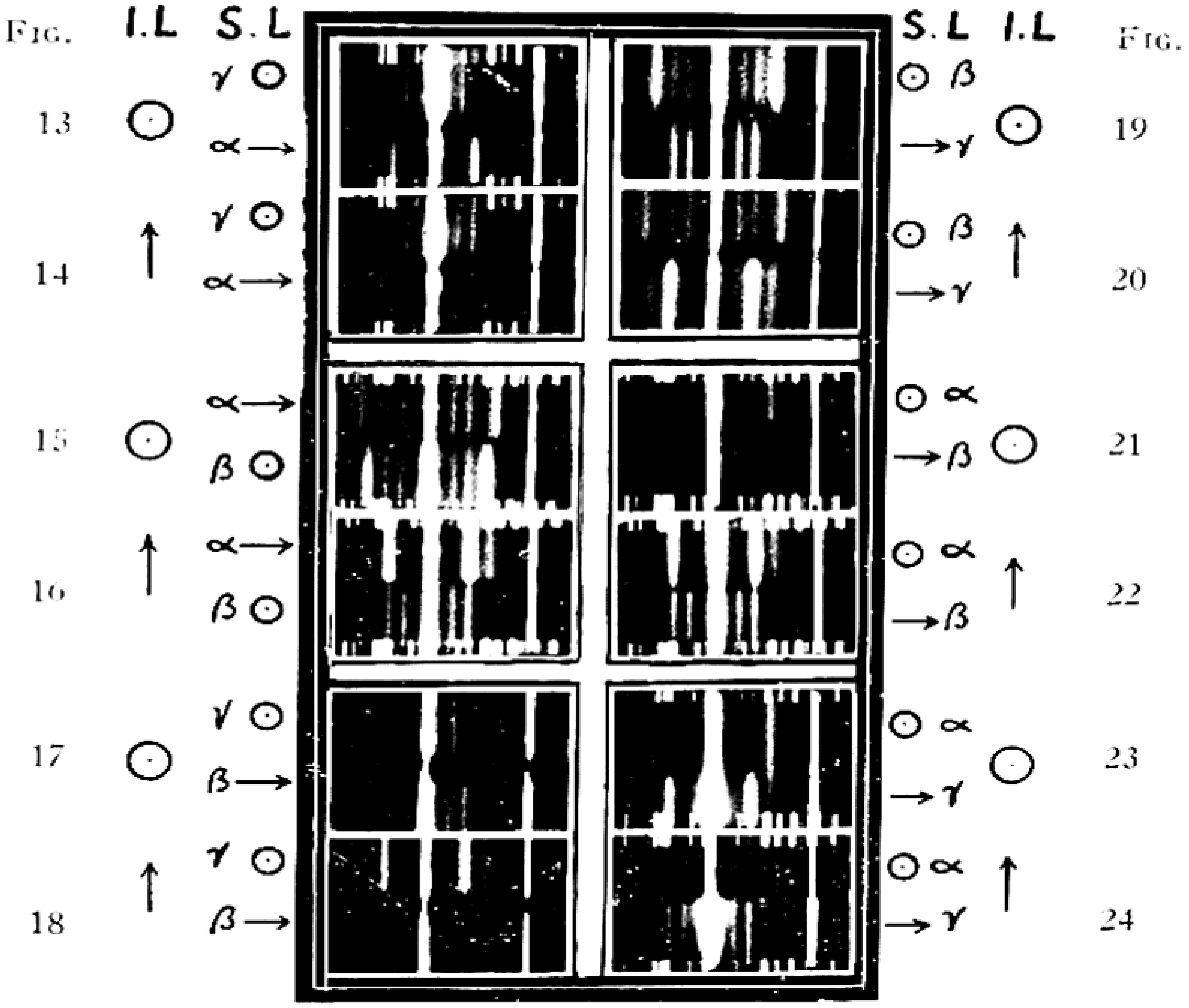
FIG.
I.L
S.L
γ ⊙
13 ⊙
α →
γ ⊙
14 ↑
α →
α →
15 ⊙
β ⊙
α →
16 ↑
β ⊙
γ ⊙
17 ⊙
β →
γ ⊙
18 ↑
β →
S.L
I.L
FIG.
⊙ β
→ γ ⊙ 19
⊙ β
→ γ ↑ 20
⊙ α
→ β ⊙ 21
⊙ α
→ β ↑ 22
⊙ α
→ γ ⊙ 23
⊙ α
→ γ ↑ 24

7. *Summary*

The paper reports the results of an exhaustive study and evaluation of 24 spectrograms concerning the Raman effect in a single crystal of naphthalene recorded for various settings of the crystal with respect to the directions of incidence and observation, and also for various directions of vibration in the incident and scattered radiations. The number and symmetry of the modes of oscillation expected of the molecule and of the crystal have been considered by application of the group theory. The experimental studies have revealed, in agreement with theory, the existence of 6 low-frequency lattice oscillations instead of the 4 reported earlier. They fall into 3 groups of close doublets, the frequencies being 38, 47; 72, 78; and 107, 121. Out of these, the lines 47, 78 and 107 are shown to be due to oscillations symmetric and the other lines 38, 72 and 121 to oscillations antisymmetric to the elements of symmetry of the monoclinic lattice. Considerations of frequency and intensity indicate that these three pairs of lines roughly correspond to rotational oscillations of the molecule about its normal breadth and length respectively. From a comparison of the data for the melt and the crystal, the frequencies of the 24 normal modes of oscillation of the molecule indicated by theory have been identified. Polarisation studies have revealed that some of the internal oscillations split up into symmetric and antisymmetric components. This splitting was clearly observable for at least two of the lines 512 and 1576 cm.$^{-1}$, in other cases, however, they were on the limit of observation or even too small to be detected. It is concluded that the polarisation behaviour of the internal oscillations also is controlled entirely by the symmetry properties of the crystal as in the case of the lattice oscillations.

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THE RAMAN SPECTRA OF ORGANIC COMPOUNDS: ANILINE

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THE complete Raman spectrum of aniline $C_6H_5 \cdot NH_2$ has not so far been obtained owing to the fact that it is highly photosensitive and turns yellow on continued exposure to light. A very intense spectrum of this substance is photographed in the present investigation by adopting a simple technique of replacing the liquid as soon as it develops a yellow tinge by freshly distilled material. The polarisation characters of the Raman lines are also obtained.

Results

The frequency shifts of the observed Raman lines and their polarisation values are listed in Table I. The spectrum and the polarisation pictures are reproduced in Plate XVII.

Aniline has been investigated previously by Bonino and Brül (1929), Ganesan and Thatte (1931), Pal and Sen Gupta (1930), Dadieu and Kohlrausch (1931), Dupont and Reymond Dulow (1936) and Vitale (1936). The results obtained by Dadieu and Kohlrausch, being more complete than of the others, are included in the table for comparison. Besides confirming the spectrum obtained by the latter authors, twenty-five new lines have been identified. The data given within brackets against the polarisation ratios are those obtained by Cabannes and Rousset (1933).

Discussion

Aniline is one of the simplest of the monosubstituted derivatives of benzene, in which the D_{6h} symmetry of benzene changes over to C_{2v} symmetry. The character table for the molecule is given in Table II.

According to this analysis, all the normal modes are single and Raman-active. It may be recalled that on account of the high order of symmetry of the benzene molecule, ten frequencies are doubly degenerate and thirteen are forbidden in the Raman effect. As the substitution of one of the hydrogen atoms by a simple group may not alter the frequency shifts of the benzene

TABLE I

No.	Authors $\Delta\nu$ in cm.$^{-1}$	ρ	Kohlrausch $\Delta\nu$ in cm.$^{-1}$	Infra-red absorption (Coblentz)
1	234 (4)	·71	234 (5)	
2	280 (0 d)	D		
3	330 (0 b)	D		
4	387 (4 b)	·63	388 (2)	
5	408 (1)	..		
6	532 (5)	·62	532 (3)	
7	619 (5)	·62		
8	700 (1 b)	..		
9	757 (3)	·71	755 (2)	
10	775 (0)	..		
11	810 (8)	·26	812 (15)	804
12	830 (8)	·30	822 (5 b)	
13	888 (0)	P		888
14	938 (1 b)	P		930
15	987 (0 d)	..		
16	996 (10)	·26 (P)	996 (10)	994
17	1029 (5)	·28	1029 (5)	1027
18	1060 (0)	..		1058
19	1110 (0)	..		
20	1149 (3)	·78		1158
21	1168 (2)	·55		
22	1200 (0)	P		
23	1230 (0)	P		
24	1272 (4 b)	·33 (·40)	1272 (4 b)	1269
25	1340 (1)	D		
26	1388 (1)	D		
27	1456 (2)	·62		
28	1499 (2)	P		1492
29	1538 (2)	P		
30	1590 (2)	D		
31	1601 (10)	·69 (·75)	1601 (10)	
32	1612 (2)	P		1626
33	2922 (2)	P		
34	3020 (1)	D		
35	3046 (10)	·53	3046 (10)	
36	3066 (4)	P		
37	3190 (1)	D		3115
38	3362 (3 b)	P	3362 (3 b)	3378
39	3423 (2 b)	D	3423 (2 b)	

TABLE II. *Character Table for* $C_6H_5{\cdot}NH_2$

C_{2v}	E	C_2	σ_v	σ_v'	n_i	n_i'	Raman	Infra-red
A_1 ..	1	1	1	1	14	13	P	*a*
A_2 ..	1	1	−1	−1	5	4	D	*ia*
B_1 ..	1	−1	1	−1	10	8	D	*a*
B_2 ..	1	−1	−1	1	13	11	D	*a*
U_R ..	14	4	6	12				
$h_j\phi_j'$ ..	42	−4	6	12				
$h_j\psi_j'$ ..	36	−2	6	12				

ring greatly, the spectrum of the derivatives provides a means of finding out these frequencies directly. The vibrations of the ring in the derivative may be classified under five groups: (1) $\omega\,(C-C)$ — vibrations of the carbon ring which are symmetric with respect to the plane, (2) $\gamma\,(C-C)$ — anti-symmetric vibrations of the ring in which the movement of the carbon ring is normal to the plane, (3) $\nu\,(C-H)$ — the valence oscillations of C — H groups, (4) $\delta\,(C-H)$ — the deformation oscillations of C—H in the plane and $\gamma\,(C-H)$ — the deformation oscillations of C—H in which the hydrogen atoms move normal to the plane of the ring. The frequencies of aniline are assigned to these groups by comparing its spectrum with those of benzene and some of its monosubstituted derivatives, *viz.*, toluene, phenol, and chlorobenzene (see Table III).

It will be observed that ν_1, the breathing frequency of benzene molecule at 993 cm.$^{-1}$, appears at 810 in aniline, the corresponding frequency for toluene being 788, for phenol 812 and for chlorobenzene 708. ν_{12} which is forbidden in benzene but appears weakly at 1006, is one of the strongest lines in the derivatives. It will also be noticed all the doubly degenerate lines in benzene are split into two lines in the latter compounds. ν_8 in benzene is a doubly degenerate frequency, which is generally attributed to the ethylenic linkage $C=C$. On account of an accidental degeneracy $\nu_1+\nu_6=\nu_8$, this is split into two nearly equally intense lines 1584 and 1605. In the derivatives, since ν_1 is lowered, this type of coincidence does not exist and hence the two lines having the above frequency shifts should be explained as due to the splitting up of ν_8. The forbidden vibration ν_{14} of benzene appears at 1612 in aniline. There are five Raman-active frequencies belonging to $\nu\,(C-H)$ which have been identified.

The infra-red absorption of aniline has been studied by Coblentz (1905) and the frequencies given by him are given in Table I. The infra-red absorptions at 804, 994, 1492, 1269 and 1626 coincide with $\omega\,(C-C)$ frequencies at 810, 996, 1499, 1272 and 1612 respectively. The Raman frequencies $\gamma\,(C-H)$, *viz.*, 888 and 938 coincide with the infra-red bands at 888 and 930, $\delta\,(C-H)$ at 1029, 1060 and 1149 coincide with 1027, 1058, and 1158, and $\nu\,(C-H)$ at 3066 and 3190 together appear as a single absorption band at 3115. This coincidence between the infra-red and the Raman spectrum is to be expected from the characteristic vibrations of the $C_{2\nu}$ symmetry.

According to the group-theoretical analysis, twenty-three out of the thirty-six vibrations should be depolarised. However it has been observed that no line is completely depolarised. The highest degree of depolarisation is ·78 for 1149, and the lowest is ·26 for 810 and 996 cm.$^{-1}$

TABLE III

Reference to vibration forms of C_6H_6	Benzene	Aniline	Toluene	Phenol	Chloro-benzene	Assign-ment
ν_4 ..	*f*	234 (3)	218 (6 b)	243 (5 b)	196 (6 b)	γ (C–C)
ν_{16}*	*f*	280 (0)			270 (½)	γ (C–C)
		330 (0)	334 (½)	..	295 (2)	γ (C–C)
ν_5 ..	400 (0)	387 (4)	..	..	..	δ (C–N)
		408 (1)		507 (½)	420 (6)	γ (C–H)
ν_6* ..	606 (5)	532 (5)	523 (5)	532 (4)		ω (C–C)
		619 (5)	622 (4 b)	620 (4)	615 (3)	ω (C–C)
	688 (½)	700 (1)	730 (0)	655 (0)	..	
ν_{18} ..	788 (0) *f*	757 (3)	..	756 (3)	..	γ (C–H)
		775 (0)	..	787 (0 b)		
		830 (8)	813 (0 b)	830 (3)	830 (0)	γ (C–N)
		888 (1 b)	978 (0)			γ (C–H)
ν_9* ..	850 (2)	938 (1 b)				
		987 (0)	993 (½)	991(0)	989 (0)	γ (C–H)
ν_1 ..	993 (10)	810 (8)	788 (10)	812 (8)	708 (6)	ω (C–C)
ν_{12} ..	1006 (½)	996 (10)	1005 (10)	1001 (10)	1003 (10)	ω (C–C)
				1013 (0)	1013 (0)	
ν_{11}* ..	1035 (0) *f*	1029 (5)	1030 (8)	1027 (8)	1024 (7)	δ (C–H)
		1060 (0)	..	1072 (1)	1121 (½)	δ (C–H)
ν_{15} ..	*f*	1110 (0)	..	1113 (0)	1158 (½)	δ (C–H)
ν_{10}* ..	1175 (2)	1149 (3)	1157 (2)	1155 (3)	1165 (0)	δ (C–H)
		1168 (2)	1181 (1)	1170 (4)	1176 (½)	δ (C–H)
		1200 (0)				
		1230 (0)				
ν_{17}* ..	*f*	1340 (1)	1348 (0)	..		γ (C–H)
		1388 (1)	1381 (1)		1372 (0)	γ (C–H)
ν_3 ..	1445 (0) *f*	1456 (2)	1402 (0)			
			1434 (0)	1425 (0)		
			1455 (0)	1464 (0)	1443 (0)	δ (C–H)
ν_{19}* ..	1480 (0) *f*	1272 (4 b)	1212 (0)	1253 (2 b)	1084 (5)	ω (C–C)
		1499 (2)	1499 (0)	1498 (½)	1565 (0)	ω (C–C)
		1538 (2)	..	..	..	δ (NH_2)
	1584 (3)	1590 (2)	1588 (0)	1595 (5)	1584 (4)	ω (C–C)
ν_8* ..						
	1605 (2)	1601 (10)	1606 (3)	1605 (5)	..	ω (C–C)
ν_{14} ..	*f*	1612 (2)	1630 (0)			ω (C–C)
			2868 (3 b)			
ν_{13} ..	*f*	2922 (2)	2922 (6 b)			ν (C–H)
ν_7* ..	3048 (4)	3020 (1)	3037 (4 b)	3017 (½)	3008 (0)	,,
		3046 (10)	3058 (8)	3051 (5)	3028 (0)	,,
ν_2 ..	3062 (8)	3066 (4 b)	3070 (4 b)	3064 (8)	3068 (10b)	,,
ν_{20}* ..	*f*	3190 (1 d)	..	3085 (½)	3140 (0)	,,
				3150 (0)	3165 (1)	,,
		3362 (3 b)	..	..	..	NH_2
		3423 (2 b)	..	..	..	

Note.—The notations employed in column one are those given by Wilson (1935).

* Denotes doubly degenerate frequencies.

The frequencies of the NH_2 group.—The NH_2 group in aniline has three normal modes of vibrations, ω_1, ω_2 and ω_3, if we assume that it possesses the form of a bent triatomic molecule. ω_2 and ω_3 come under the symmetric class and should be highly polarised, and ω_1 is antisymmetric and hence depolarised. All the three are active in the Raman and the infra-red spectra; but while ω_2 is the strongest in the former, it is the weakest in the latter. From our knowledge of the spectra of H_2O and H_2S, we should expect ω_1 and ω_2 to appear in the region 3300 and ω_3 to be nearly half of ω_2. Indeed there are two lines observed at 3362 and 3423, the former being polarised and the more intense of the two and the latter depolarised. 3423 has therefore to be assigned to ω_1, and 3362 to ω_2. The infra-red absorption at 3398 reported by Coblentz has to be attributed to ω_1. The Raman line at 1538 which does not belong to the benzene ring is obviously ω_3. A similar line at 1537 in urea $CO(NH_2)_2$ is attributed by Ananthakrishnan (1937) to the same mode of vibration in NH_2 group. Applying the formula given by Dennison (1926) and assuming the above frequencies for ω_1, ω_2 and ω_3, we get the force-constant for N—H as $6 \cdot 3 \times 10^5$ dynes/cm. and the angle HNH as 104° 48′.

The C—N frequencies.—Besides the frequencies of the benzene ring and the NH_2 group we should expect three Raman frequencies, *viz.*, one valence oscillation of the C—N linkage, one deformation oscillation of C—N in the plane and one deformation oscillation perpendicular to the plane. Assuming the force-constant of C—N as $4 \cdot 85 \times 10^5$ dynes/cm. (Hibben, 1939) the valence frequency comes out as 1040 cm.$^{-1}$ Venkateswaran and Bhagavantam (1930) from their studies on methyl and ethyl amines conclude that the line at 1050 is due to this linkage. According to Medárd (1935) this frequency varies from 910 to 850 in nitro-compounds. In compounds CH_3NH_2, $(CH_3)_2NH$ and CH_3N, it falls at 1047 (7), 930 (5), and 850 (5) respectively. Thus we see that the Raman frequency characteristic of the C—N linkage is very much influenced by the constituent group. From the analysis of the spectrum of aniline given in Table III, we have to conclude that the polarised line 830 (8) is the valence and the line 408 (1) is the deformation frequency in the plane of the ring.

Besides the lines assigned above, there are five other lines, *viz.*, 700 (1), 775 (0), 987 (1), 1200 (0) and 1230 (0) which require explanation. 987 is presumably due to ν_1 vibration of the carbon isotope C_{13}, 775 due to $2\nu_5$ and the others due to combinational frequencies.

In conclusion the authors wish to thank Sir C. V. Raman for his keen interest in the work.

Summary

An intense Raman spectrum of aniline has yielded thirty-nine lines. They are: 234 (4, ·71), 280 (0, D), 330 (0, D), 387 (4, ·63), 408 (1), 532 (5, ·62), 619 (5, ·62), 700 (1,), 757 (3, ·71), 775 (0), 810 (8, ·28), 830 (8, ·30), 888 (0, P), 938 (1, P), 987 (0), 996 (10, ·26), 1029 (5, ·28), 1060 (0,), 1110 (0), 1149 (3, ·78), 1168 (2, ·55), 1200 (0, P), 1230 (0, P), 1272 (4, ·33), 1340 (1, D), 1388 (1, D), 1456 (2, ·62), 1499 (2, P), 1538 (2, P), 1590 (2, D), 1601 (10, ·69), 1612 (2, P), 2922 (2, P), 3020 (0, D), 3046 (10, ·53), 3066 (4, P), 3190 (1, D), 3362 (3, P), and 3423 (2, D). Thirty of these are assigned to the benzene ring by comparing these frequencies with those of benzene and its monosubstituted derivatives. 3362 (3 P), 3423 (3 D,) and 1538 (2 P) are assigned to the NH_2 group and 830 (8, ·30) and 408 (1) to the C – N linkage.

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THE RAMAN SPECTRA OF ORGANIC COMPOUNDS: DIETHYL DISULPHIDE

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INVESTIGATIONS on the Raman spectra of organic polysulphides are comparatively few, and no attempt appears to have been made to determine the state of polarisation of the lines. Using ten grams of pure freshly distilled liquid, a very intense spectrum of diethyl disulphide and its polarisation are obtained and the results are discussed in the present paper in relation to its structure.

Results

The observed frequency shifts and their polarisation characters are given in Table 1. The values of frequencies of the intense lines are correct to ± 1 cm.$^{-1}$ For the weak lines which could not be observed in the measuring microscope, the shifts are estimated with reference to an iron arc comparison spectrum and are correct to ± 5 cm.$^{-1}$ The state of polarisation of weak lines for which the deflection in the microphotometric curve is very small is given as either polarised (P) or depolarised (D). The photographs of the spectrum and its horizontal and vertical components are reproduced in Plate XVII.

Ethyl disulphide has been investigated by Venkateswaran (1931) and by Douzelot and Chaix (1936) and their results are also given in Table I.

Discussion of Results

The discussion of the Raman spectra of organic sulphur compounds by earlier investigators is wholly confined to the determination of frequencies corresponding to C–S, S–S and S–H linkages. In the case of thioethers, there is general agreement in the assignment of a sharp and intense line at about 640 cm.$^{-1}$ to C–S binding and the lines at 506 and 189 cm.$^{-1}$ to S–S oscillations wherever they exist. It is significant that the Raman frequency of 506 in diethyl disulphide which is intense and highly polarised, has nearly the same value as the polarised Raman line at 470 and that at 189 corresponds to the intense depolarised line at 150 cm.$^{-1}$

TABLE I

Raman frequencies of diethyl disulphide

No.	Authors $\Delta\nu$ cm.$^{-1}$	Polarisation	Venkateswaran 1931	Douzelot and Chaix (1936)	Assignments
1	115 (4)	D	..	..	Chain
2	189 (7)	·71	..	179 (w)	,,
3	197 (3)	·80	..	..	,,
4	259 (1 d)	D	..	..	,,
5	295 (1 d)	P	..	..	,,
6	324 (1 d) (double)	·60	333 (0)	..	,,
7	357 (2 d)	D	384 (0)	..	,,
8	400 (1)	..	..	..	,,
9	458 (1)	P	..	..	,,
10	506 (7)	·32	509 (6)	507 (w)	,,
11	520 (4)	·25	525 (3)	522 (w)	,,
12	578 (1)	..	..	..	,,
13	649 (10)	·57	641 (8)	639 (st)	,,
14	668 (5)	·48	667 (4)	663 (w)	,,
15	756 (2)	P	764 (0 d)	..	,,
16	969 (4 b)	·79	967 (4 d)	964 (w)	,,
17	1033 (2)	D	1033 (0)	..	(C_2H_5)
18	1052 (5)	·45	1052 (4)	1045 (v.w)	Chain
19	1125 (1)	P	..	1142 (w) 1187	(C_2H_5)
20	1257 (3)	·57	1260 (1 b)	..	Chain
21	1294 (1)	..	..	..	(C_2H_5)
22	1417 (3)	·84	1422 (2)	1420 (w)	,,
23	1444 (3)	·86	1454 (2 d)	1446 (w)	,,
24	2874 (4)	·30	2871 (4)	2873 (m)	,,
25	2911 (3)	·54	2911 (4 d)	..	,,
26	2931 (8)	·59	2930 (8)	2923 (m)	,,
27	2973 (4)	·78	2969 (4 b)	..	,,

in molten sulphur (Venkateswaran, 1936). By analogy with sulphur, these frequencies can be treated as the valence and the deformation frequencies of the S–S bond. The presence of these two lines in ethyl disulphide supports the conclusion arrived at by Venkateswaran (1931) that S–S is connected by a single bond.

The presence of this single bond in polysulphides raises the interesting question of the existence of 'free rotation' in these compounds about the S–S bond. This problem of free rotation about a single bond in liquids has been examined by several authors from the point of view of the Raman effect. Theoretically, the *trans* configuration has the minimum potential energy and is therefore the most stable. But due to thermal energy, the molecule can be rotating about the stable position or between the *cis* and *trans* forms. It is also assumed that the latter case is equivalent to free rotation about the single bond. Extensive experimental investigations on the problem have been undertaken by Kohlrausch and his collaborators

(1935) and by Mizushima, Morino and others (1934–1936) with ethane derivatives. Recently, Ananthakrishnan (1937) has also given some attention to this problem. Kohlrausch and others (1933) have observed that these compounds yield a greater number of Raman lines than is to be expected from a purely *trans* state and have come to the conclusion that there is no free rotation as such, but the *cis* and the *trans* types of molecules co-exist in them. From a series of investigations carried out by Mizushima, Morino and Higashi on the Raman effect and dipole moment of ethane derivatives, they come to the conclusion that the intra-molecular state is far from that corresponding to the 'free rotation' in its literal meaning and in some cases (solids) they have found a state corresponding to the 'frozen rotation' in which all the molecules settle themselves in a *trans* state. According to the latter authors, the greater number of Raman lines observed is to be explained as arising from the disturbance of the symmetry of the *trans* form by the interaction of the C–C bond with other valence bonds.

The only compound of sulphur which has been investigated for observing the possibility of free rotation about S–S bond is S_2Cl_2 by Morino and Mizushima (1937). These authors have used the green and the yellow radiations of the mercury arc as exciting lines. Since the scattering power of these lines is small, only the intense Raman lines have been recorded by them. The spectrum cannot, therefore, be considered as sufficiently complete to draw any definite conclusion regarding the free rotation about the S–S bond. The two compounds, $(CH_3)_2S_2$ and $(C_2H_5)_2S_2$, are more suitable for investigation as 4046 and 4358 A.U. radiations could be made use of for excitation. The structural formula of dimethyl disulphide could be written as $H_3C{-}S{-}S{-}CH_3$ and that of diethyl disulphide as $H_5C_2{-}S{-}S{-}C_2H_5$. To a first approximation, we may separate out the vibrations of the C–H bonds from the chain of carbon and sulphur atoms. The chain may be straight or symmetrical *trans* type, or it may be asymmetrical *cis* type. For methyl disulphide as the former two forms possess a centre of symmetry, only three of the six normal modes of vibrations are allowed in the Raman effect; for the *cis* form, all the six are active. Venkateswaran (1931) has reported nine lines for this compound, of which five may be assigned to the chain and four to the CH_3 group. The polarisation characters of these lines are not known. From the data available, it is not possible to draw any definite conclusion and a more exhaustive investigation appears desirable. We could not undertake this investigation as the liquid was not available.

In the case of diethyl disulphide, there are six atoms in the chain $C_2{-}S{-}S{-}C_2$ and we should expect six polarised Raman lines for the straight chain and for the *trans* form. For the *cis* form, there should appear twelve Raman lines, half of which should be depolarised. If the chain is zigzag without any element of symmetry, there will be twelve Raman lines, all of them being polarised. Of the twenty-seven lines recorded for ethyl disulphide, the lines 1052, 1125, 1294, 1417, 1444, 2874, 2911, 2931 and 2973 can be easily identified as the frequencies of C_2H_5 groups, by a comparison of its spectrum with those of ethyl alcohol, diethyl ether and diethyl amine. The remaining eighteen lines are due to the chain. This total number of lines due to the chain is more than should be expected either for a pure *trans* or a pure *cis* symmetry or to the loss of symmetry of the *trans* form due to resonance as shown by Mizushima and his co-workers. The presence of five lines which are more or less completely depolarised, *viz.*, 115, 197, 259, 357 and 969 is significant, suggesting the existence of the *cis* molecule in the liquid. The *trans* configuration is, on the other hand, revealed by the presence of highly polarised lines in its spectrum. It will be observed that the intense lines due to S–S in the region of 506 and 189 and due to C–S in the region of 649 cm.$^{-1}$ are accompanied in each case by lines of medium intensity and having nearly the same polarisation characters. We may, therefore, attribute the lines at 189, 506 and 649 to the *trans* form and those at 197, 520 and 668 to the *cis* form. Theoretically for the same mode of oscillation which is symmetric, the Raman line due to the *trans* form will be more intense than of the *cis*. Hence, from the recorded intensity of the above lines, we can conclude that the two types of the molecules co-exist in nearly equal proportions. If there is free rotation about the S–S bond in the molecule, we should expect a wing to accompany the intense lines of the chain similar to the rotation wing accompanying the Rayleigh line in liquids; but no such wing was observed in the spectrum of ethyl disulphide, indicating that free rotation as such does not exist.

The authors take this opportunity to thank Sir C. V. Raman for his encouragement in the course of the work.

Summary

An intense Raman spectrum of diethyl disulphide and its polarisation characters are recorded. The spectrum consists of twenty-seven lines. Nine of these are observed for the first time. It is shown that nine of these lines (three of which are depolarised) belong to the ethyl group (C_2 H_5), and the remaining eighteen of which six are depolarised belong to the chain C_2–S–S–C_2. The results are discussed in relation to the problem of ' free rotation ' about the S–S bond. It is concluded that six polarised lines are due to the *trans*

and twelve due to the *cis* forms; and that these two types of molecules co-exist in the liquid in equal proportions.

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THE RAMAN SPECTRA OF ORGANIC COMPOUNDS : BINARY LIQUID MIXTURES

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IT is now well established that the marked blue opalescence of binary liquid mixtures at the critical solution temperature is due to the formation of molecular clusters of size comparable to the wave-length of light. In order to find out the exact nature of these aggregates, an investigation of the Raman spectra of such mixtures has been undertaken. Two typical systems are chosen. They are made up of (1) a polar and a non-polar liquid, *viz.*, cyclohexane and aniline, and (2) two polar liquids, *viz.*, iso-butyric acid and water. The critical mixture of cyclohexane and aniline contains 54% by weight of the former and 46% of the latter, the critical temperature being 30° C. and of water and isobutyric acid contains 50% by weight of each, the critical temperature being 26° C. The two liquids are immiscible below the critical temperature. In each case the liquids are mixed together in the proper proportion and distilled over completely into the experimental tube. The tube is heated by a cylindrical electric heater and when the critical temperature is attained, the liquids are thoroughly mixed up by shaking to form a homogeneous fluid, and this temperature is maintained throughout the exposure. The spectra of the two liquids and their mixture are recorded separately. Since the unmodified scattering is very intense in the case of the critical mixtures, their Raman spectra are accompanied by a fairly strong continuous background. In fact, due to this latter cause, Bogros and Rocard (1928) and Martin (1928) failed to record any Raman line for a critical mixture of phenol and water, and Ziemecki and Jodko (1929) for a mixture of *iso*-butyric acid and water. In the case of cyclohexane-aniline mixture, this background is considerably suppressed and the discolouration due to photo-decomposition is prevented by using a solution of sodium nitrite as filter. For *iso*-butyric acid-water mixture, the spectra were obtained with unfiltered radiation as well as with 4047 A.U. alone by using a filter of iodine in CCl_4 and with 4358 A.U. by using the nitrite filter. The spectrum of the mixture in each case was compared with those of the component liquids both by superposition and by careful comparison with the iron arc spectrum recorded alongside of every picture.

Results

The results of the investigation are given in Tables I and II. In the case of *iso*-butyric acid, the polarisation characters of the spectrum of the pure liquid and of the mixture were also studied and are recorded in the table. The spectrum of *iso*-butyric acid-water mixture taken with 4046 A.U. radiations of the arc is reproduced in Plate XVII along with that of the pure acid.

TABLE I. *Cyclohexane – Aniline Mixture*

Cyclohexane	Aniline	Mixture	Cyclohexane	Aniline	Mixture
..	234 (4)	234 (1)	1348 (1)	1340 (1)	1342 (0)
384 (½)	387 (4 b)	387 (2)	1442 (5 b)	..	1445 (2)
426	..	..	..	1456 (2)	1456 (0)
600	532 (5)	532 (1)	..	1499 (2)	..
..	619 (5)	619 (0)	..	1538 (2)	..
..	757 (3)	757 (0)	..	1590 (2)	..
802 (10)	..	802 (3)	..	1601 (10)	1601 (6)
..	810 (8)	810 (5)	..	1612 (2)	1612 (0)
..	830 (8)	830 (5)	2854 (10 b)	..	2854 (5)
..	996 (10)	996 (5)	2922 (8 b)	..	2922 (4)
1029 (6)	1029 (5)	1029 (3)	..	3046 (10)	3046 (5)
1156 (3)	1149 (3)	1149 (1)	..	3066 (4)	3066 (2)
..	1168 (2)	1162 (1)	..	3362 (3 b)	3362 (1)
1265 (5)	1272 (4 b)	1270 (4)	..	3423 (2 b)	3423 (0)

TABLE II. *Iso-Butyric Acid-Water Mixture*

Iso-butyric Acid	Polarisation	Mixture	Polarisation	*Iso*-butyric Acid	Polarisation	Mixture	Polarisation
130 (2)	D	..		1224 (2 b)	P	..	
253 (2)	D	253 (0)		1234 (0)		..	
342 (2 b)	D	342 (1)	D	1253 (0)		..	
435 (1)		..					
510 (5)	P	Disappears		1300 (2)	D	1300 (1)	
		519 (2 b)	P	1313 (0)		..	
540 (1)	D	540 (3)	D	1430 (2)	P	Disappears	
603 (2)	D	603 (1)	D	1457 (5 b)	D	1453 (4)	D
690 (0)		..		1654 (4 b)	P	Disappears	
710 (1)		..				1715 (2 b)	D
743 (2)	P	743 (3)	P	2732 (1)		..	
800 (10)	P	800 (4 b)	P	2763 (2)		..	
		Broader and weaker					
854 (1)	D	..		2815 (0)			
909 (5)	D	909 (5)	D	2874 (6)	P	2874 (5)	P
930 (0)				2920 (4)	P	2920 (2)	P
962 (3)	D	962 (3)	D	2978 (6)	D	2978 (4)	D
991 (1)	D	..					
1010 (0)		..					
1042 (1)		..					
1092 (2 b)		1092 (1)					
1106 (2 b)		1106 (1)					

Discussion of Results

1. *Cyclohexane–aniline mixture.*—It will be noticed from Table I that all but the very weak lines of the two molecules have been recorded in the mixture. There is neither any shift of frequencies, nor any change in the relative intensities of the lines. It is, however, observed that in spite of the fact that cyclohexane forms 61% by volume (56% by weight) of the mixture, its spectrum is very much less intense than that of aniline as judged from the intensities of lines in the neighbourhood of 800 cm.$^{-1}$ In the mixture, the spectra of the liquids are photographed under identical experimental conditions, and this difference in the intensity of the Raman lines due to the same mode of vibrations is presumably due to the lower scattering power of cyclohexane. As the spectrum of the mixture is only a superposition of the spectra of the two liquids, we have to conclude that the inter-molecular forces between the molecules forming clusters should be assumed to be too weak to influence the intra-molecular vibrations to any extent.

2. *Iso-butyric acid-water mixture.*—The striking changes that take place in the Raman spectrum of *iso*-butyric acid when it forms a critical mixture with water are the disappearance of three strong lines 510 (5), 1430 (2) and 1654.(4 b) and the appearance of two broad lines at 519 (2 b) and 1715 (2 b). The Raman band at 3460 of the pure water is shifted slightly towards higher frequency in the mixture. These changes are illustrated by the microphotometric curves given in Fig. 1 and indicated by arrows in the spectra of the acid and the mixture. The most intense and well polarised line of the acid at 800 cm.$^{-1}$ is also slightly broadened and rendered relatively weak, while the line 909 has gained somewhat in intensity. These variations suggest that unlike cyclohexane-aniline mixture, *iso*-butyric acid molecule undergoes configurational changes when it forms a critical composition mixture with water. It has been shown by Sunanda Bai (1940) that when pure *iso*-butyric acid is heated to its boiling point the line at 1654 which is due to the carbonyl linkage, weakens and a new broad line 1726 makes its appearance. These changes are attributed to the breaking up of some of the dimer molecules into single molecules at the higher temperature. The hydrogen bond formed between C=O and O-H in the dimer lowers the carbonyl frequency from its normal value of 1726 to 1654. The disappearance of the line at 1650 and the appearance of a line at 1720 in its place has also been observed by Edsall (1936) in aqueous solutions of formic and acetic acids and by Saxena (1940) in trichloro-acetic acid and explained on the same basis as given above. Saxena (1940) has also shown that the carbonyl frequency of the monomer at 1720 is polarised and of the dimer at 1650 is depolarised. These observations are fully supported by the

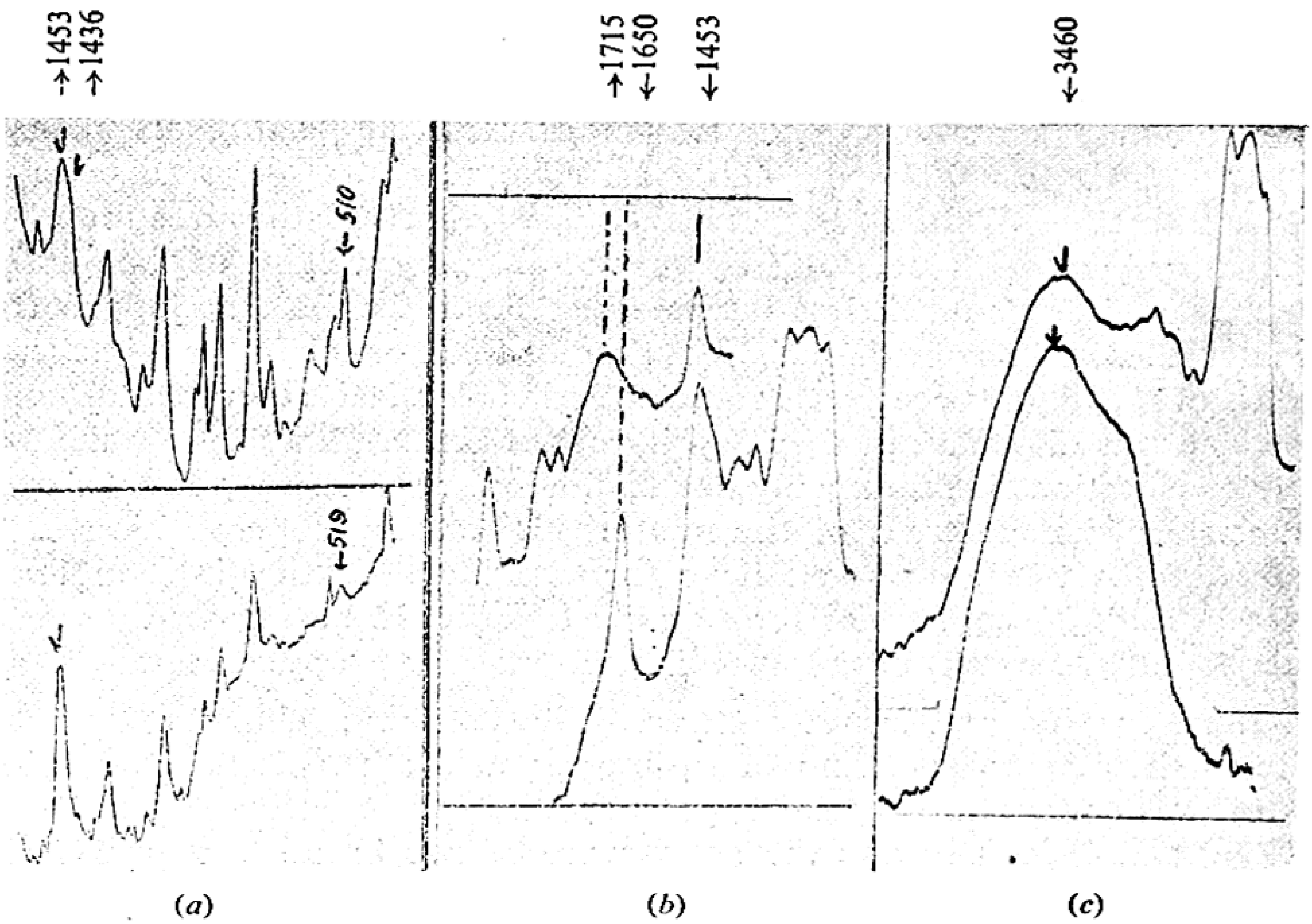

FIG 1. Microphotometric records of horizontal and vertical components for *iso*-butyric acid at room temperature.

(*a*) Above : Pure Acid
Below : Mixture

(*b*) Below : Pure Acid
Above : Mixture

(*c*) Below : Pure Water
Above : Mixture

polarisation measurements of these lines in the present investigation. Besides, according to Saxena, we should expect one polarised line at about 1400 for the dimer corresponding to the symmetrical oscillation of the carboxyl group. The line at 1436 in *iso*-butyric acid is polarised and is evidently to be assigned to this mode of vibration of the dimer, and its disappearance in the critical solution mixture is readily understood as arising from depolymerisation. The changes taking place for the line at 510 is analogous to that observed by Edsall in dilute aqueous solutions of formic and acetic acids and by Saxena for trichloroacetic acid. In formic acid the line at 678 (3) is replaced by 708 (1 b) in 35% aqueous solution, in acetic acid the line at 623 (4) by 630 (3 b) in 33% solution and in trichloroacetic acid, the line at 675 by a diffuse one at 695. It should, however, be mentioned that the lines 678 of formic acid and 623 of acetic acid are depolarised according to Saxena (1940), while we have observed that the line 506 of *iso*-butyric acid is partially polarised. The changes in this region are also due to the dissociation of the acid molecule to smaller units.

RAMAN SPECTRA OF LIQUIDS

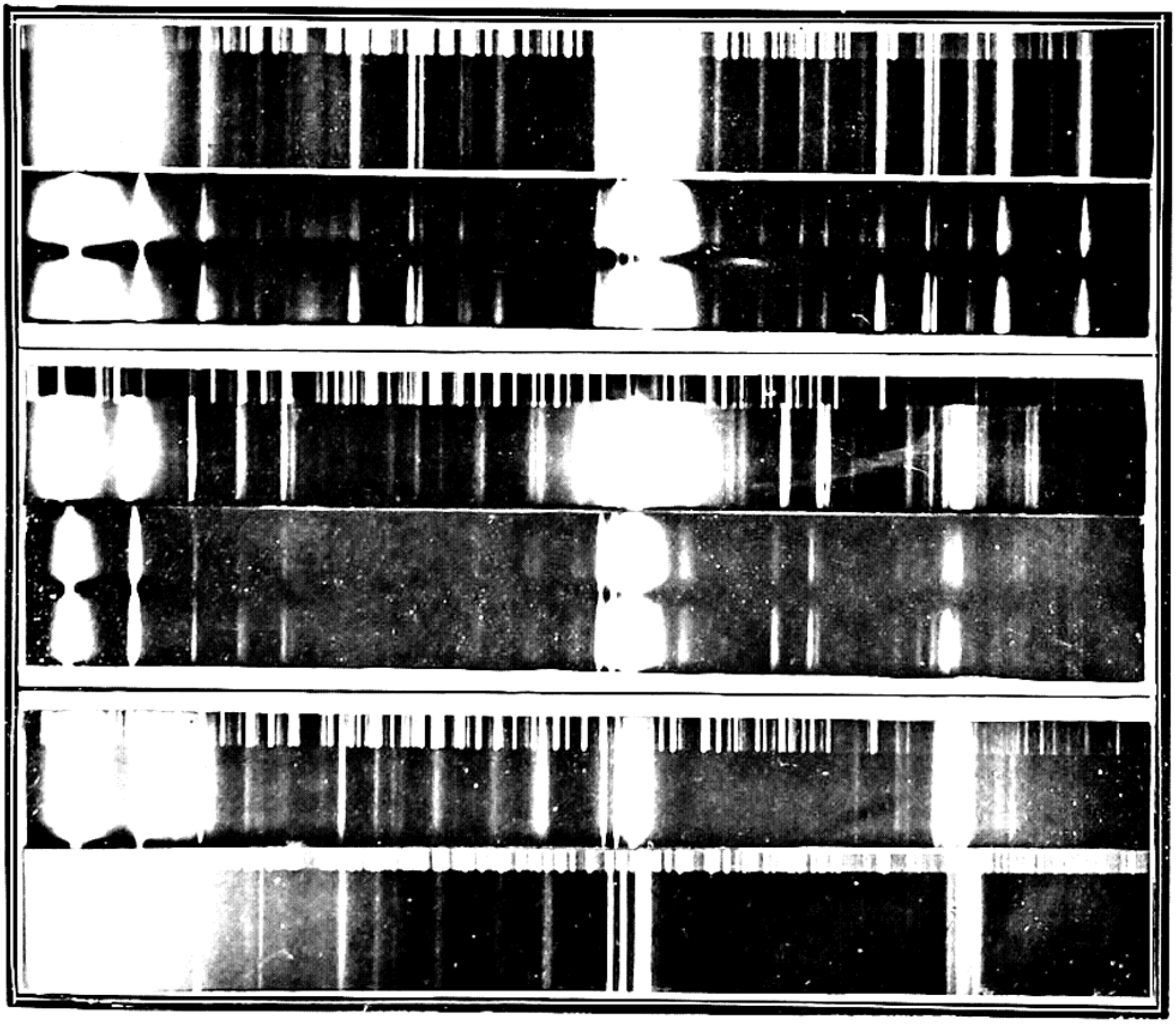

FIG. 1. (*a*) Aniline; (*b*) Polarisation of Aniline
FIG. 2. (*a*) Diethyl disulphide; (*b*) Polarisation of Diethyl disulphide
FIG. 3. (*a*) *Iso*-butyric Acid; (*b*) *Iso*-butyric acid-Water mixture

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Since the changes in the spectrum mentioned above can be brought about only by an interaction of the acid and the water molecules, we have to conclude that *iso*-butyric acid which is immiscible with water below 26° C, forms an intimate solution above that temperature accompanied by the attendant changes such as depolymerisation and dissociation. The opalescence of the critical mixture should, therefore, arise from clusters composed of molecules of the acid and water together. The hydrogen bond in the dimer in the pure acid presumably opens up, resulting in effect in the simultaneous formation of single molecules and of weaker bonds between the latter and the water molecules in larger numbers. This also accounts for the shift of the water band at 3460 cm.$^{-1}$ to a higher frequency.

The polarisation characters of the intense lines in *iso*-butyric acid remain the same in the mixture so far as could be ascertained. The hydroxyl frequency does not appear in the pure acid. Four new lines, *viz*., 1234, 1253, 1313 and 2763 cm.$^{-1}$ are observed for the liquid in addition to those reported by Sunanda Bai (1940).

Summary

The Raman spectra of two critical solution mixtures, namely cyclohexane-aniline and iso-butyric acid-water, are obtained and compared with the spectra of the component liquids. No changes are observed in the cyclohexane-aniline mixture. In the *iso*-butyric acid-water mixture the following changes are observed: Three fairly intense lines at 510, 1430 and 1654 cm.$^{-1}$ of the acid disappear in the mixture and instead, broad lines appear at 519 and 1715. The strongest line of the acid at 800 cm.$^{-1}$ becomes slightly broader and less intense. The strong water band at 3460 appears to be shifted to a slightly higher frequency. From a comparison of these changes with those reported for formic, acetic and trichloroacetic acids, it is concluded that at the critical temperature, the acid molecules change over from dimer to monomer state. This indicates that at or above the critical temperature, the two liquids in the mixture become homogeneous as in solutions. The results are discussed in relation to the cluster formation in the binary liquid mixtures.

In conclusion we wish to place on record our thanks to Prof. C. V. Raman for his interest in the work.

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THE SCATTERING OF LIGHT IN EMULSIONS

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1. *Introduction*

It is readily verified that the droplets of liquid contained in a dilute emulsion are spherical in shape and isotropic in structure. The problem of the scattering of light by such a medium was dealt with rigorously by Mie (1908) in a well-known paper. According to this theory when the size of the droplets is comparable with the wave-length of light, the scattering becomes asymmetrical, the intensity of light scattered in the forward direction being greater than that in the backward direction. This accords well with the experimental observations of Schæfer and Mirzkirch (1923), Schæfer and Wilmsen (1924) and Krishnan (1934). Further, the Mie theory indicates that if the incident beam is polarised with vibrations vertical or horizontal, the light scattered in the transverse horizontal direction should be completely polarised with its vibrations vertical or horizontal respectively. This fact has also been verified experimentally by Krishnan (1938) for the case of dilute emulsions in which the secondary scattering is negligible. Another important conclusion arrived at from the theory of Mie is that the light scattered by large spherical particles when the incident light is polarised, would in directions other than those parallel and perpendicular to the incident electric vector, be elliptically polarised. Thus, if the nicol polarising the incident beam assumed to traverse the medium in a horizontal direction is rotated so that the vibrations change over from the vertical to the horizontal direction, the light scattered transversely in a horizontal direction would be plane polarised in the two extreme positions of the nicol and elliptically polarised in the intermediate positions.

The degree of ellipticity would be a function of the size of the particles and of the inclination of the plane of polarisation of the incident beam to the vertical. This aspect of the problem of light scattering by emulsions does not appear to have been experimentally studied so far. It was therefore thought desirable to investigate the nature of the scattered light with the incident light polarised in different azimuths, for the case of dilute emulsions. For the case of concentrated emulsions the process of scattering becomes more complicated than that envisaged in the Mie theory, due to the presence of what is known as secondary scattering. Some interesting phenomena observed regarding the state of polarisation of the secondary scattering in a moderately concentrated emulsion are also included in this paper.

2. *Optical Arrangements*

The experimental technique for detecting and measuring the ellipticities of the scattered light is essentially the same as that described by Sir C. V. Raman (1941) in a recent paper. The light from a powerful carbon arc was rendered parallel by means of a lens. Immediately following the lens, a glass cell with plane parallel end plates containing a solution of alum was placed to cut off the heat rays. Next to the cell was mounted a second lens of long focal length. A nicol mounted on a graduated circle was placed in the path of the beam of light emerging out of the second lens. By rotating this nicol, the beam could be polarised with vibration direction inclined at any desired angle with the vertical. The light emerging through the nicol was focussed at the centre of a small narrow rectangular cell containing the emulsion under investigation. The four sides of the cell were covered with black paper except for three small windows, one for the entrance of light, the second for its exit and the third for observation. A Babinet compensator was placed in the path of the transversely scattered light, its principal plane being inclined at 45° to the plane of observation. The scattered light was finally viewed through a nicol and an eye-piece. The nicol was oriented so as to transmit vibrations which had their electric vector horizontal.

3. *Preparation of Emulsions*

Three different emulsions were prepared for the study, namely (1) olive oil in water, (2) linseed oil in water and (3) toluene in water. The emulsions were prepared as follows:—A small but measured quantity of the oil in each case was poured into a known volume of double distilled water to which were added a few milligrams of sodium oleate. The whole mixture was well stirred and passed through a homogenizing mill so as to get an emulsion with droplets of uniform size. In order to reduce the average particle size of the droplets, the emulsion was passed through the mill a large number of times. By varying the number of times a particular emulsion was put through the emulsifier, it was possible to prepare different samples of the same emulsion containing droplets of size varying from sample to sample, but more or less uniform in each. The average particle size was measured in every case under a microscope. In all the cases the emulsions were sufficiently dilute to avoid the effects of secondary scattering.

4. *Some Preliminary Observations*

In a typical case when the incident beam was polarised with vibrations vertical, a system of fringes was observed distinctly through the compensator, the cross-wire of the same falling on a dark fringe. As the nicol polarising the incident beam was slowly turned round from the vertical, *i.e.*, as θ* was increased from 0°, the fringe system appeared to remain stationary. For further rotation of the nicol in the incident beam, the fringe system shifted laterally and the cross-wire appeared to move gradually from the dark fringe to the bright fringe, showing thereby that the scattered light was elliptically polarised to a measurable degree. As θ was increased further, the shifting of the cross-wire continued and finally when the incident beam was polarised with vibrations horizontal, *i.e.*, $\theta = 90°$, the cross-wire coincided with one of the bright fringes. It is evident from the foregoing results that in the case of dilute emulsions, when the incident light is vertically polarised, the transversely scattered light is polarised with vibrations vertical. As the plane of polarisation of the incident light is rotated away from the vertical, the vertical and horizontal components of the scattered light have a phase difference and the scattered light is elliptically polarised. The phase difference between the two components increases continuously for further rotation of the plane of polarisation of the incident beam. As θ approaches 90°, the scattered light is again plane-polarised with the vibrations horizontal.

The effect of concentration on the nature of light scattered by emulsions was then examined. It was found that when the concentration was rather low, *i.e.*, when there was no disturbance due to secondary scattering, the fringes were very clear for the two limiting values of θ namely 0° and 90°. The range of variation of θ over which the shift of the cross-wire from the dark to the bright fringe took place increased with increasing concentration. When the concentration of the emulsion could no longer be considered as low, the fringe system became less distinct for $\theta = 0°$ and 90° as it was then superposed on a bright background due to secondary scattering. Moreover, the shift of the cross-wire from the dark fringe became visible for a lower value of θ. As the concentration was further increased it was found that the fringe system was split into two separate systems, in one the cross-wire being in the centre of the bright fringe and in the other it being in a different position. When the concentration was as high as 0·25% the visibility of the fringes was very poor and one could not observe any shift of the cross-wire. When the concentration was raised to 1% no fringes were visible for all values of θ, showing thereby that the scattered light was completely depolarised.

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*θ is the inclination of the direction of vibration in the incident beam to the vertical.

Some preliminary observations were also made with ordinary suspensions. It was then found that as θ was increased from 0°, *i.e.*, as the plane of polarisation of the incident beam was slowly rotated from the vertical, the fringe system became less bright but with the cross-wire coinciding with a dark fringe. For a particular value of θ depending upon the nature of the colloid under investigation, the cross-wire suddenly appeared in the centre of a bright fringe and remained there for further increase in the value of θ. For $\theta = 90°$, the fringe system was again bright and distinct. The author was thus unable to detect any trace of ellipticity in the light scattered by suspensoids.

5. *Factors influencing Ellipticity*

In order to measure the ellipticity of the light scattered by emulsions the following procedure was adopted. The eye-piece used for visual observation was removed and the scattered light as seen through the compensator nicol combination was photographed. From the photograph the position of the cross-wire was noted and its distance from the nearest dark fringe was measured. Assuming the phase difference to be equal to π corresponding to a shift of the cross-wire from the dark fringe to the next bright fringe, the phase difference between the two components of the scattered light corresponding to any intermediate position of the cross-wire could be easily evaluated.

(*a*) *Influence of the nature of the dispersed phase.*—The ellipticity of the light scattered in the transverse horizontal direction was measured in the manner described above for olive oil in water, linseed oil in water and toluene in water emulsions. A red filter was used in the path of the incident beam. The results obtained are graphically represented in Fig. 1. The refractive indices of olive oil, linseed oil and toluene are 1·466, 1·480, 1·498 respectively. Judging from the results obtained from the oil in water emulsions alone, one might conclude that as the refractive index of the dispersed phase increases, the ellipticity curve shifts towards lower values of θ.

(*b*) *Influence of droplet size.*—Different samples of the same emulsion were prepared containing droplets of two different sizes. The ellipticity of the scattered light was determined in every case using a red filter in the path

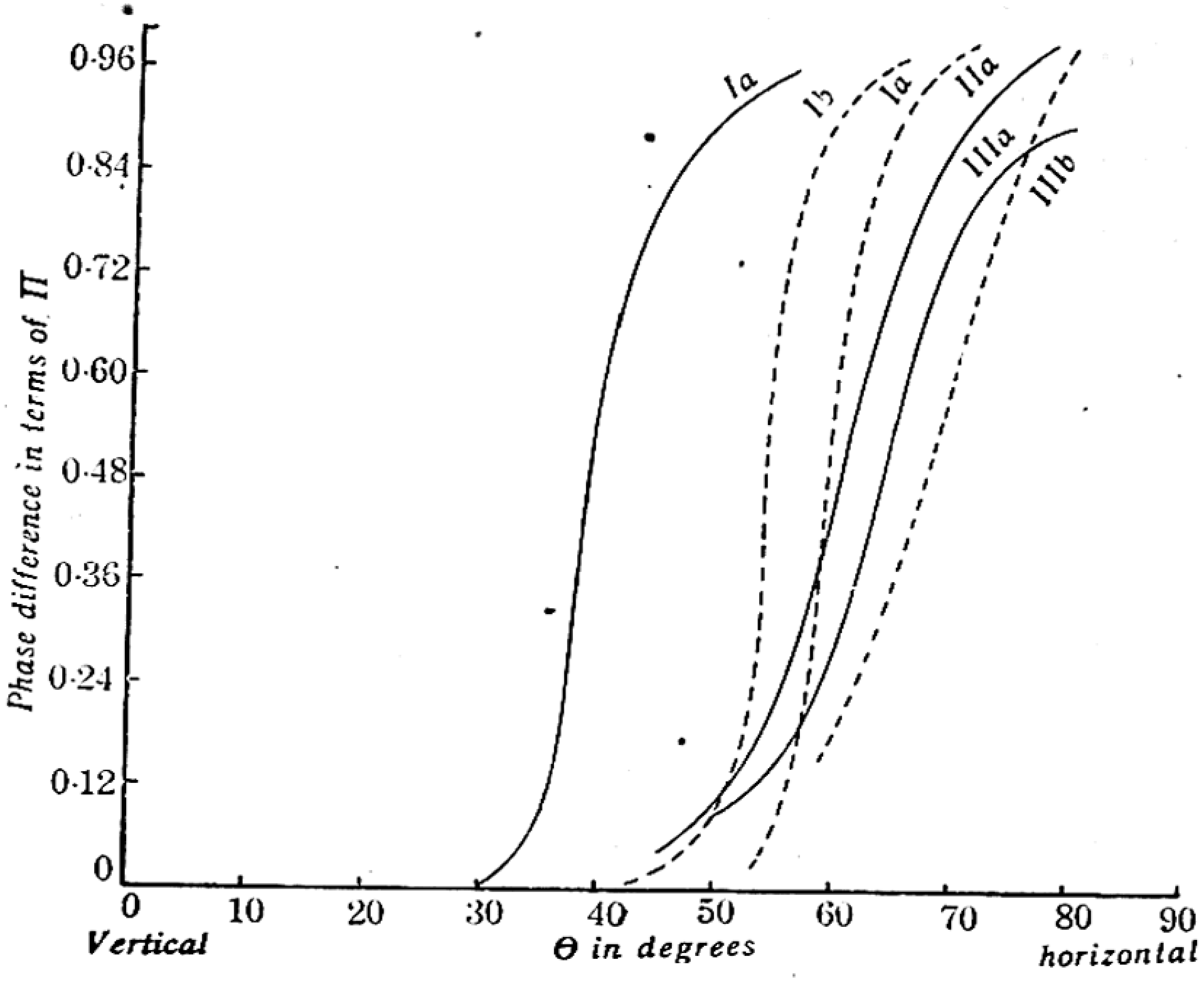

FIG. 1

I *a*	Linseed oil emulsion droplet size	2·67 μ
I *b*	,, ,,	4·02 μ
II *a*	Olive oil emulsion droplet size	2·67 μ
II *b*	,, ,, ,,	3·43 μ
III *a*	Toluene emulsion droplet size	3·01 μ
III *b*	,, ,, ,,	2·94 μ

of the incident beam. The dependence of ellipticity on droplet size is shown graphically in Fig. 1. The general conclusion is that the ellipticity curve shifts towards higher values of θ as the size of the droplets increases.

(*c*) *Influence of wavelength of the incident light.*—The ellipticity of light scattered by linseed oil and olive oil emulsions was measured for different regions in the visible spectrum using suitable coloured filters in the path of the incident beam. The results obtained with a blue filter (mean transmission 4700 A.U.) and a red filter (mean transmission 6500 A.U.) are given in Fig. 2. For any particular inclination of the plane of polarisation of the incident light with the vertical, the ellipticity of the scattered light increases with decreasing wave-length of the light used.

(*d*) *Influence of the angle of scattering.*—The ellipticity of the scattered light in the case of olive oil emulsion was determined for the following

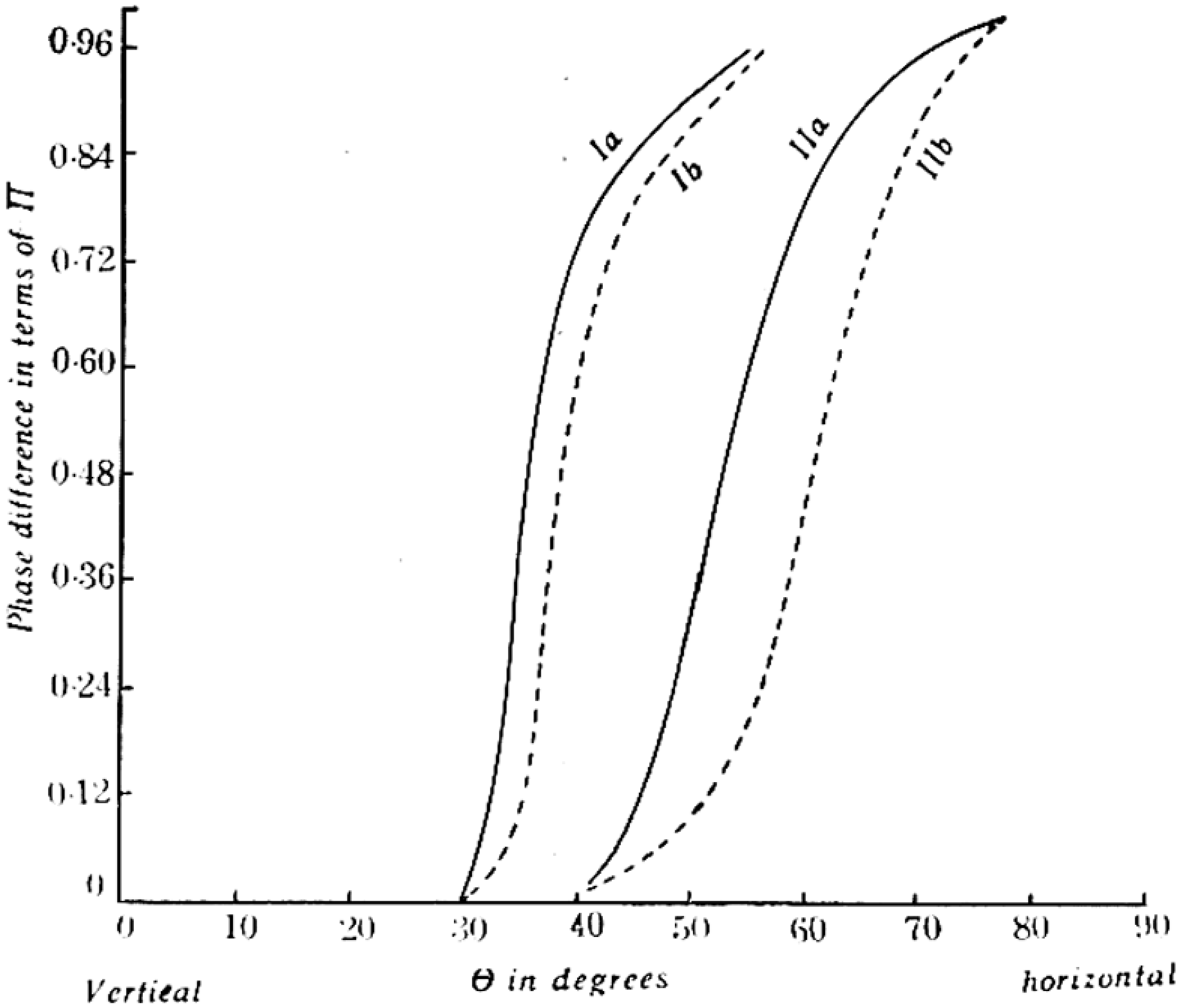

FIG. 2

I *a*	Linseed oil	emulsion	blue filter	(Mean transmission 4700 A.U.)
I *b*	,,	,,	red ,,	(,, 6500 A.U.)
II *a*	Olive oil	,,	blue ,,	(,, 4700 A.U.)
II *b*	,,	,,	red ,,	(,, 6500 A.U.)

values of the angle of scattering, 40°, 55°, 60°, 90° and 100°, using red light. The results are represented graphically in Fig. 3. The general trend of the results appears to be that as the angle of scattering increases the ellipticity curve shifts in the direction of increasing value of θ for $\theta < 90°$. For $\theta > 90°$ the ellipticity curve shifts in the opposite direction. For any particular orientation of the plane of polarisation of the incident beam, the ellipticity of the scattered light is a minimum for the transverse direction and increases as one moves away from the transverse direction on either side.

6. *Polarisation of Secondary Scattering*

Using the same optical arrangement as before but without the Babinet compensator, a series of photographs was taken of the light scattered in the transverse direction by a moderately concentrated emulsion for different orientations of the analysing nicol with the incident light polarised with

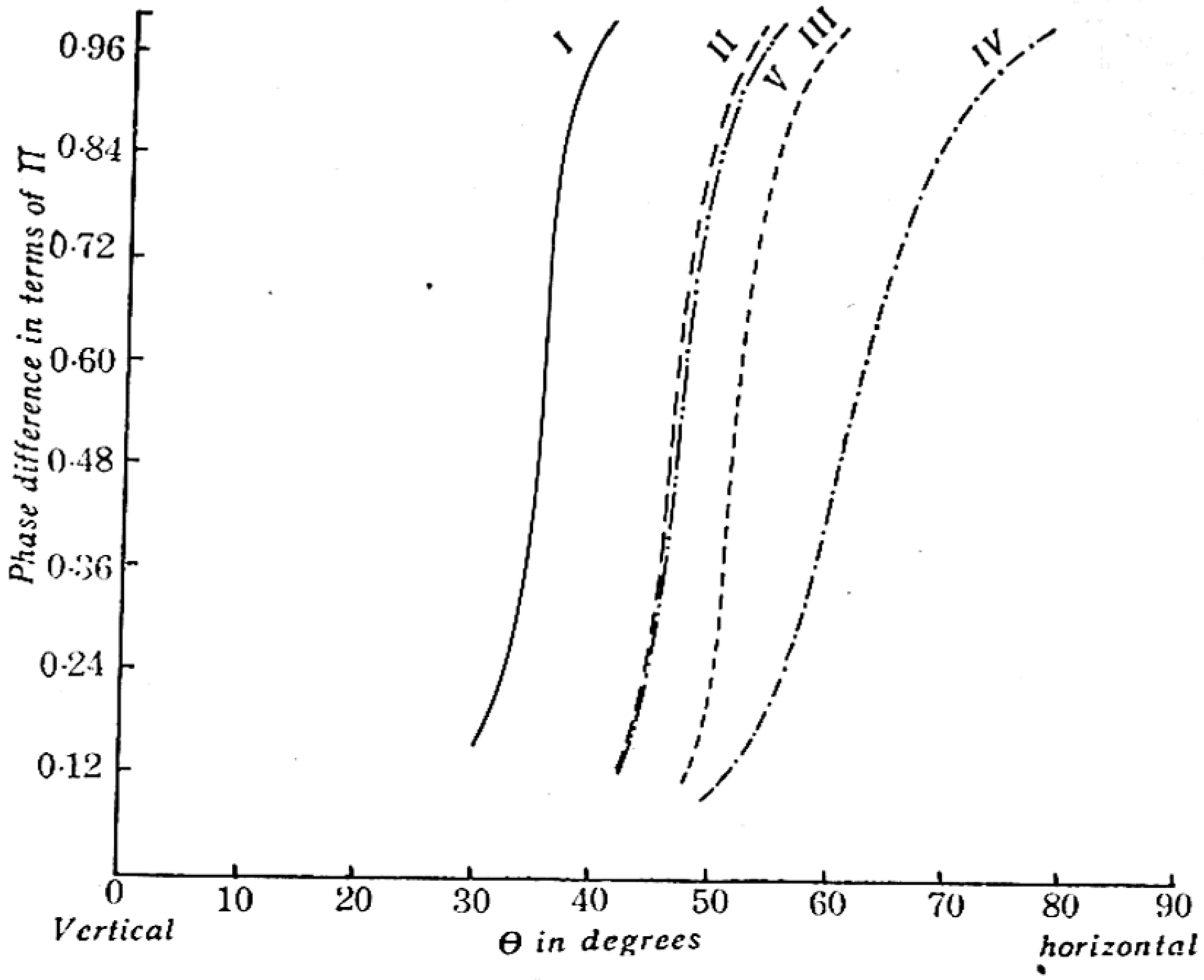

FIG. 3.

Ellipticity of scattered light in olive oil emulsion (droplet size = 2·67 μ)

I for angle of scattering = 45°
II ,, = 50°
III ,, = 60°
IV for angle of scattering = 90°
V ,, = 100°

vibrations vertical. The photographs are reproduced in Plate XVIII. Fig. 4 in the Plate shows the photograph taken with the principal plane of the analyser vertical. In this position it is not possible to separate the primary track from the background illumination arising from secondary scattering and scattering of higher orders. The primary scattering and the secondary scattering in the immediate neighbourhood which go to make up the diffuse spot (seen in Fig. 4) are vertically polarised. The diffuse spot is symmetrical with respect to the direction of the incident beam. As the analyser is rotated counter-clockwise, the diffuse cone of light shifts to one side of the central track (see Fig. 5) and after a certain stage a weak diffuse cone appears on the other side of the central track (see Fig. 6). When the analyser is oriented with its principal plane horizontal, two bright streaks in the form of a fork are seen starting from the point at which the light enters the emulsion (see Fig. 7). The fork is symmetrically situated with respect to the position of the central track. As the

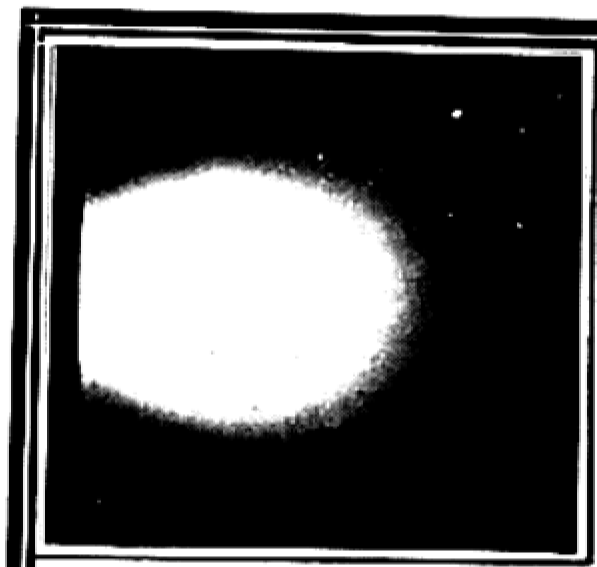

Fig. 4

Principal plane
of analysing nicol
vertical

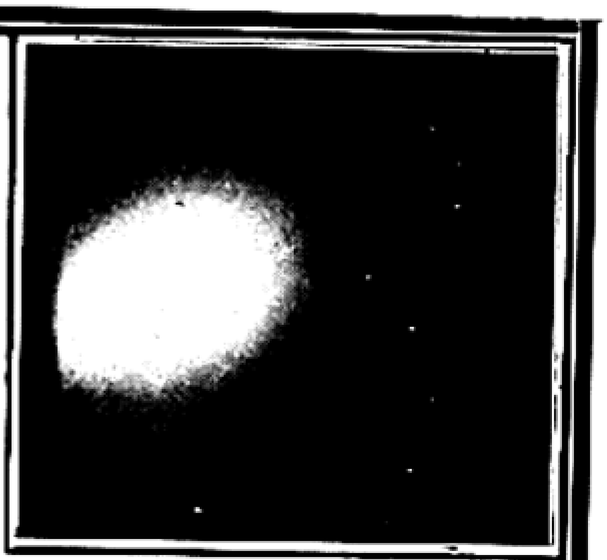

Fig. 5

Principal plan
at 70°
with vertical

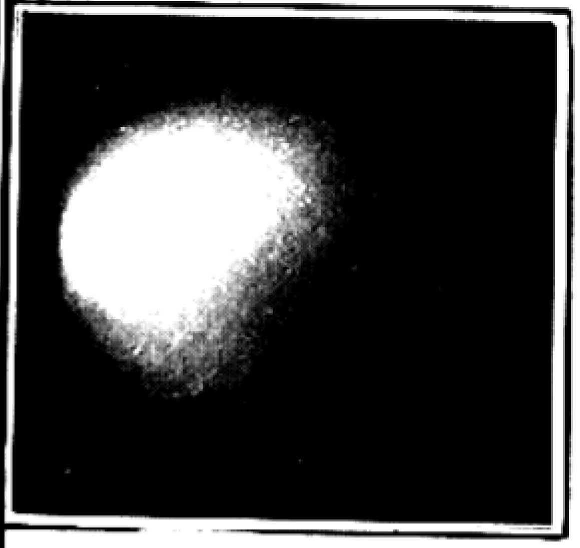

Fig. 6

Principal plane
at 80°
with vertical

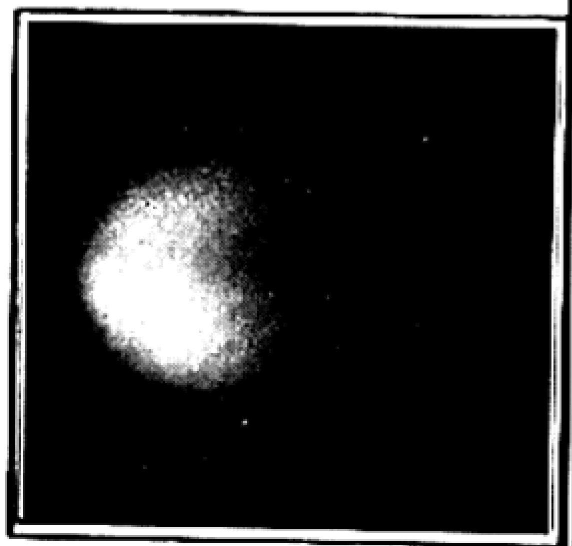

Fig. 7

Principal plan
at 90°
with vertical

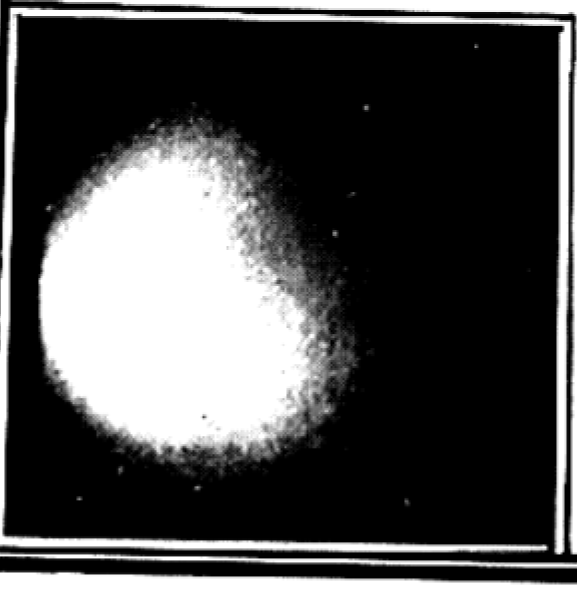

Fig. 8

Principal plane
at 100°
with vertical

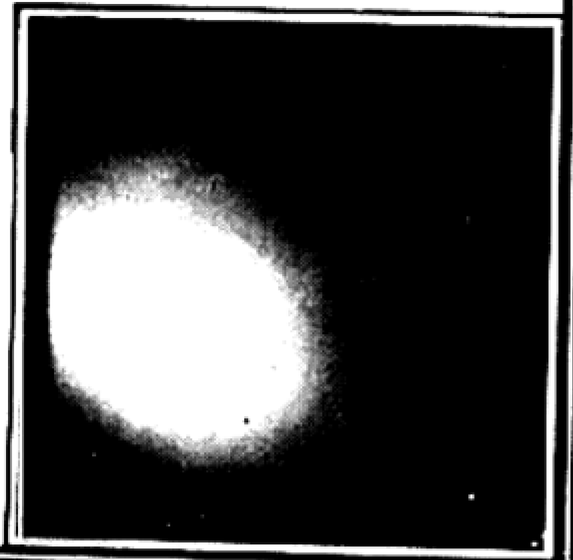

Fig. 9

Principal plane
at 110°
with vertical

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analysing nicol is rotated further, the whole phenomenon is repeated with the difference that the bright diffuse cone now appears on the other side of the central track. Similar results are also obtained for incident light polarised with vibrations horizontal. In the case of a highly concentrated emulsion it was not possible to detect any difference in the intensity of background illumination for various orientations of the analysing nicol.

In conclusion, the author is very much indebted to Prof. Sir C. V. Raman for his kindness in suggesting the problem and for taking keen interest in it.

7. *Summary*

Investigations have been made regarding the nature of the light scattered by emulsions using a nicol for polarising the incident beam in any desired azimuth and a Babinet compensator for analysing the scattered light. It is found that in the case of dilute emulsions the light scattered in the transverse horizontal direction is in general elliptically polarised. The dependence of ellipticity on the inclination of the plane of polarisation of the incident light to the vertical, the nature of the dispersed phase, the size of the droplets, the wave-length of the incident light and also the angle of scattering has been investigated in some detail. The phase difference between the vertical and horizontal components of the scattered light is a minimum for observation in the transverse direction and it increases as one moves away from it on either side. In the case of concentrated emulsions the scattered light is highly depolarised irrespective of the state of polarisation of the incident beam. Some interesting phenomena regarding the state of polarisation of secondary scattering in the case of moderately concentrated emulsions are also illustrated in the paper.

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THE FLUORESCENCE OF THE URANYL COMPOUNDS AND THE RAMAN SPECTRUM OF THE URANYL ION

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1. *Introduction*

ONE of the remarkable facts about the fluorescence spectrum of solid uranyl salts is that it consists of a series of eight discrete bands having a constant wave number separation of 860 cm.$^{-1}$ These bands lie between 4700 and 6300 A.U., the intensity being a maximum for the middle two lying in the region of 5000 and 5400 A.U. The absorption spectrum of these salts, on the other hand, runs in the opposite direction, *viz.*, towards the ultra-violet, the spacing between the consecutive bands being about 710 cm.$^{-1}$, which is less than that in fluorescence. Both the absorption and the emission bands split up into several sharp lines at liquid air temperature. While the main fluorescence and absorption bands may be assumed to owe their origin to the electronic transitions of the hexavalent uranium atom in the uranyl group (Nichols and Howes, 1919), the mechanism responsible for the subsidiary bands is not well understood. The constancy of the band-spacing and the smaller shift of the absorption bands suggest that the internal vibrations of the UO_2^{++} ion give rise to these bands, the vibrational lines associated with the ground state taking part in the emission spectrum and those associated with the first excited level, in the absorption. Evidence regarding this assignment of the bands is furnished by the Raman and the infra-red spectra of uranyl salts obtained by Conn and Wu (1938). These authors have observed one intense Raman line at 860 cm.$^{-1}$ and a weak one at 210 cm.$^{-1}$; while the infra-red absorption has yielded two frequencies at 860 and 930 cm.$^{-1}$ The principal frequency at 860 cm.$^{-1}$ coincides with the wavenumber separation of the emission bands. It was thought desirable to obtain an intense Raman spectrum of uranyl chloride solution and the state of polarisation of the lines in order to find out the structure of the UO_2^{++} ion and to identify the mode of vibration which modulates the electronic transitions giving rise to fluorescence.

2. *Experimental Arrangements*

A saturated solution of uranyl chloride was prepared and rendered fairly dust free by several filtrations. As the blue radiations of the mercury arc are strongly absorbed by the solution, Hg 5461 A.U. was used as the exciting line. The fluorescence of the solution appearing in the green was inhibited by adding a few drops of KBr solution as suggested by Conn and Wu. Uranyl chloride has the advantage over the other uranyl salts of being not intensely fluorescent. The yellow lines of the mercury arc were suppressed from the incident light by using a filter of didymium chloride solution surrounding the tube. Two horizontal air-cooled pyrex mercury arcs were placed on either side of the Raman tube. The transversely scattered light was analysed by a Żeiss three-prism glass spectrograph. Five days exposure was required to record an intense Raman spectrum on Ilford panchromatic HP_2 plates. The lines were measured as usual in comparison with an ion arc spectrum. As the light from the arcs had to be focussed on the experimental tube by large condensers for polarisation studies and the scattered light was further weakened during transmission through the double-image prism, fifteen days exposure was required to obtain a fairly intense polarisation picture.

3. *Results and Discussion*

The Raman spectrum obtained in the present investigation is reproduced in Figs. I *a* and I *b* in Plate XIX. The Raman frequencies with the visual estimates of their intensities are given in Table I. The single line reported by Conn and Wu at 210 appears as a close doublet and the intense line at 865 is accompanied by a faint companion whose frequency shift is visually estimated as 853. The line 865 is highly polarised as may be seen from Fig. I *c*.

TABLE I. *Raman frequencies for Uranyl chloride: Exciting line*, 5461 *A.U.*

No.	Wave-length in A.U.	Raman shift in cm.$^{-1}$	Intensity	Conn and Wu.		Assignments
				Raman	Infra-red	
1	5520	197	2	210	..	ν_2
2	5529	226	2			
3	5727	853	0	..	..	..
4	5731	865 P	10	860	860	ν_1
5	5746	909	1	..	930	ν_3

If the binding between UO_2^{++} and Cl_2^{--} ions in the uranyl chloride is electrovalent, it cannot give rise to Raman lines and all the frequencies observed would have to be attributed to the uranyl group. The presence of additional components for ν_1 and ν_2 however suggests that the dissociation of the salt may be incomplete.

The fact that the UO_2 ion gives rise to three main Raman lines indicates that it has a bent structure as in H_2O, SO_2 or H_2S. A bent triatomic molecule possesses three single Raman-active internal vibrations, namely the symmetrical ν_1, the deformational ν_2 and the asymmetric ν_3. By analogy with the known spectra of triatomic molecules, we may assume that $\nu_3 > \nu_1 > \nu_2$. Thus putting $\nu_1 = 865$, $\nu_2 = 211$ and $\nu_3 = 909$ cm.$^{-1}$, the force constant between U and O and the angle O–U–O are calculated using the equations given by the valence force field theory (Penney and Sutherland, 1936). These values are $f\,(\mathrm{U{-}O}) = 6 \cdot 97 \times 10^5$ dynes/cm. and $\mathrm{O{-}\hat{U}{-}O} = 140°$. It may be remarked here that Fankuchen (1936) has concluded from X-ray analysis of certain uranyl acetates that the UO_2 group is linear. As however, the scattering power of the oxygen atoms is weak compared with the uranium atom, it is probable that the X-ray studies cannot give decisive results.

Summary

The Raman spectrum of a saturated solution of uranyl chloride has been observed to consist of three lines having frequency shifts of 211 cm.$^{-1}$, 865 cm.$^{-1}$ and 909 cm^{-1}. The intense line at 865 cm.$^{-1}$ is highly polarised and accompanied by a faint companion. The lowest frequency line at 211 cm.$^{-1}$ is also found to be a doublet. From the appearance of the Raman lines in the compound it has been concluded that the UO_2^{++} ion has a symmetrical bent structure. The frequency shift of 865 cm.$^{-1}$ coincides with the wave number separation of the fluorescent bands in the solid, suggesting that the subsidiary bands in fluorescence arise from the modulation of the principal electronic transition by the symmetric vibration of the uranyl group.

In conclusion, I would like to express my gratitude to Sir C. V. Raman for the guidance he has given me throughout the work. I would like to thank Dr. C. S. Venkateswaran and Mr. P. G. N. Nayar for their kind assistance.

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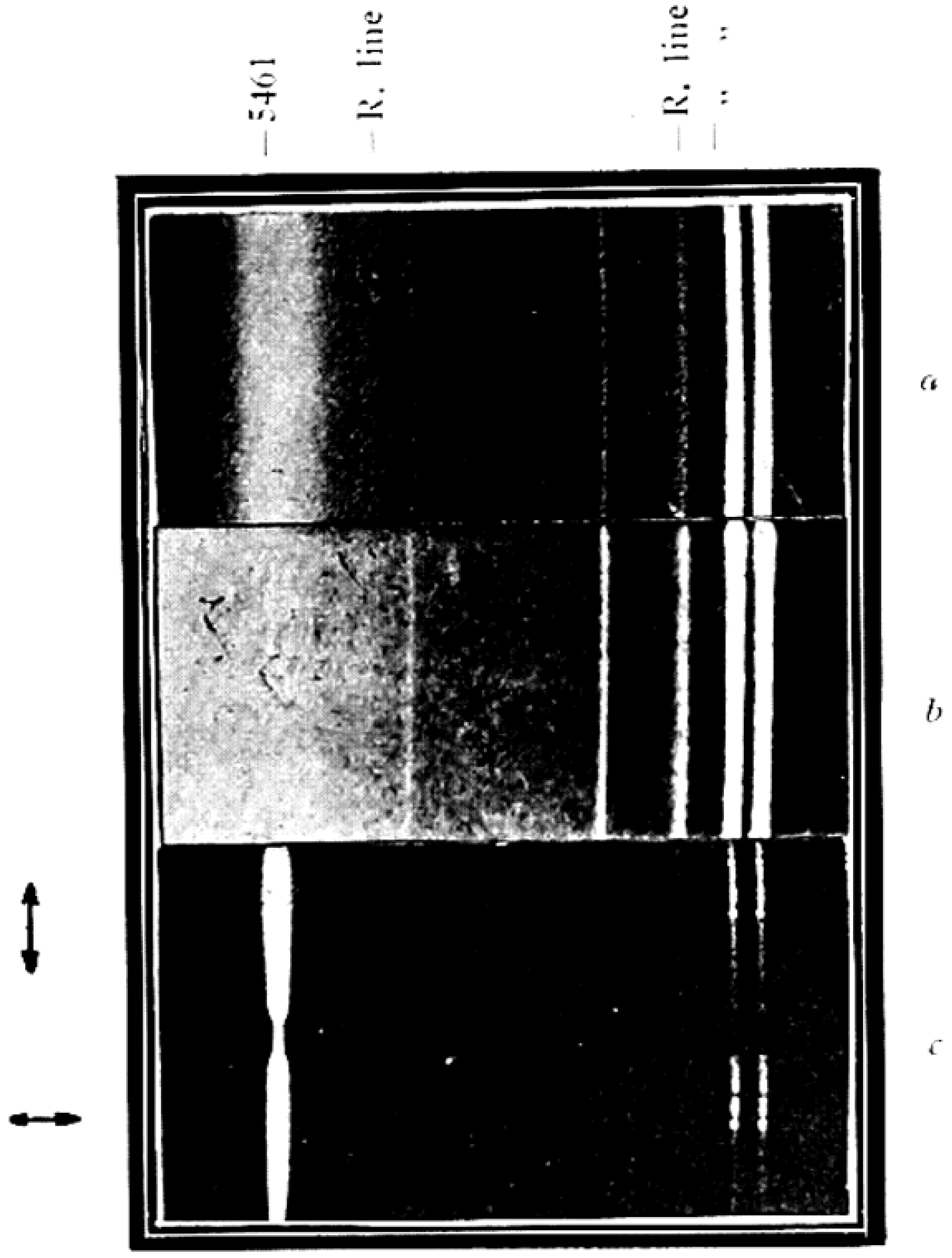

Fig. 1. Raman Spectrum of UO_2Cl_2

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